

Descriptors for High-Energy Nitro Compounds; Estimation of Thermodynamic, Physicochemical and Environmental Properties

Michael H. Abraham,^{*,[a]} William E. Acree, Jr.,^[b] and Xiangli Liu^[c]

Abstract: We have used a variety of physicochemical systems, including water-solvent partitions, solubility in non-aqueous solvents, and HPLC and gas chromatographic retentions to obtain descriptors for nitro compounds and high energy compounds. These descriptors can then be used to predict a wide range of other physicochemical properties as well as thermodynamic and environmental properties. We illustrate the latter by predictions of the va-

por pressure of sublimation, the enthalpy of sublimation and the heat capacity of sublimation at 298.15 K, and predictions of human skin permeability from water. With respect to the obtained descriptors, the most startling finding is that cyclic high energy compounds, with no 'active' hydrogen atom, have a substantial 'hydrogen bond' acidity. We suggest that this is due to electron-deficient ring systems that act as Lewis acids.

Keywords: High-energy compounds · Gas-solvent partition coefficients · Water-solvent partition coefficients · Vapor pressure · Enthalpy of sublimation

1 Introduction

There is considerable interest in the properties of 'high energy' nitro compounds, especially with regard to their environmental fate. Thus properties such as solubility, water-phase, and gas-phase partitions, and vapor pressure are of considerable importance in deducing the fate of these compounds. Individual physico-chemical properties have been predicted, such as the enthalpy of sublimation [1] and vapor pressure [2], and there have been predictions of a number of properties of high-energy compounds [3–6]. The usual approach is to obtain an algorithm to correlate data for a given process using a set of calculated descriptors, and then to use the calculated descriptors for high-energy compounds to predict further values. Thus a new algorithm is required for each different process.

Sandler et al. [7] adopted a different approach altogether. They used Abraham solute descriptors [8–10], calculated through the ABSOLV program [11], together with previously-determined equations [12,13] to estimate water-solvent partitions, P , for a number of high-energy nitro compounds. However, the ABSOLV descriptors did not yield very good predictions. Sandler et al. [7] then used the COSMO method to calculate the coefficients in equations for water-solvent partitions and used these equations to obtain better values of the Abraham descriptors. Di Toro et al. [8] made a significant step forward; they determined water-solvent partition coefficients in five systems for eight compounds and used this data to calculate 'experimental' Abraham parameters. However, there is considerable additional experimental data available that can be used to obtain

Abraham descriptors for the eight compounds, and other nitro and high-energy nitro compounds as well. We, therefore, assembled as much data as we could, including the data from Di Toro et al. [8], in order to obtain more rigorous Abraham descriptors for the eight compounds and to obtain Abraham descriptors for other such compounds. Finally, we can use our determined descriptors to estimate further values in a large number of physicochemical and thermodynamic processes.

[a] M. H. Abraham
Department of Chemistry,
University College London,
20 Gordon St, London WC1H, 0AJ, UK
*e-mail: m.h.abraham@ucl.ac.uk

[b] W. E. Acree, Jr.
Department of Chemistry,
1155 Union Circle Drive #305070,
University of North
Texas, Denton,
TX 76203-5017, USA

[c] X. Liu
School of Pharmacy and Medical Sciences,
Faculty of Life Sciences,
University of Bradford, Bradford
BD7 1DP, UK
*e-mail: X.liu18@bradford.ac.uk

2 Methodology

Our method is based on two general linear free energy relationships, Eqs. (1) and (2), that can be used to correlate and to predict the transfer of neutral solutes from water to organic solvents and from the gas phase to organic solvents. The dependent variable in Eq. (1) is $\log P$, where P is the molar water to solvent partition coefficient for a series of solutes, and in Eq. (2) is $\log K$ where K is the dimensionless gas phase to solvent partition coefficient for a series of solutes [10,13,14]. The method has been reviewed several times [9,10,15–17].

$$\log P = c + e E + s S + a A + b B + v V \quad (1)$$

$$\log K = c + e E + s S + a A + b B + l L \quad (2)$$

In Eq. (1) and (2) the independent variables, or descriptors, are properties of the neutral solutes as follows [13–17]: E is the solute excess molar refraction in $\text{cm}^3 \text{mol}^{-1}/10$, S is the solute dipolarity/polarizability, A is the overall solute hydrogen bond acidity, B is the overall solute hydrogen bond basicity, V is McGowan's characteristic molecular volume in $\text{cm}^3 \text{mol}^{-1}/100$ and L is the logarithm of the gas to hexadecane partition coefficient at 298 K. The coefficients in Eq. (1) and Eq. (2) are shown in Table 1 for partition from water and from the gas phase to the relevant solvents that we shall encounter [12–15,18].

As well as using direct water-solvent partition coefficients, we can also use solubilities in non-aqueous solvents S_s . These can be transformed into water to (dry) solvent partition coefficients through Eq. (3) where S_w is the solubility in water. In Table 1 we give the coefficients in equations for water to dry solvent partitions. We denote 'wet' solvents as 'w', dry solvents as 'd', and solvents that take up so little water that coefficients for wet and dry solvents are the same as 'wd'.

$$P = S_s/S_w \text{ or } \log P = \log S_s - \log S_w \quad (3)$$

Values of P obtained directly or from solubilities can be transformed into corresponding gas to solvent partition coefficients, K_s , through Eq. (4), where K_w is the gas to water partition coefficient.

$$K_s = P \cdot K_w \text{ or } \log K_s = \log P + \log K_w \quad (4)$$

The values of $\log P$ and $\log K_s$ for a given solute can then be used to construct a set of simultaneous equations that can be solved for the unknown descriptors E , S , A , B , V , and L and the (usually) unknown value of $\log K_w$. If a required value of $\log S_w$ in Eq. 3 is not known, it can be treated as another unknown to be obtained through solution of the simultaneous equations. The 'Solver' add-on to the Microsoft Excel program provides a particularly convenient method for the solution of these simultaneous equations.

Since the number of equations is always larger than the number of unknowns, a trial-and-error procedure is adopted to obtain the unknowns that give the best-fit to the equations. The 'Solver' add-on uses the smallest standard deviation between observed and calculated dependent variables as a criterion of 'best-fit'.

It is a considerable advantage to be able to deduce the value of some of the descriptors, and hence to reduce the number of unknown descriptors that have to be obtained. For neutral organic compounds, the McGowan volume, V , can easily be calculated [9,19], and can be obtained from available sources [11,20]. The E -descriptor can be calculated from a liquid refractive index, n , at 293 K and a value of V [9]. If such a value is unavailable, n can be calculated [21] and E itself can be calculated [11,20].

Eq. (4) is particularly useful. Di Toro et al. [8] measured $\log P$ for a number of compounds in five water-solvent systems and constructed a set of five simultaneous equations to obtain the descriptors S , A , and B . However, we can use Eq. (4) to deduce five additional values of $\log K_s$. We also have two additional equations in $\log K_s$ itself, see Table 1, and so from five $\log P$ values, we can obtain no less than 12 simultaneous equations for the calculation of S , A , B , L , and $\log K_w$. This is very significant, because $\log K_w$, the inverse of Henry's constant, is an important physicochemical and environmental parameter [14].

3 Results and Discussion

We first start with the compounds used by Di Toro et al. [8] for which four or five $\log P$ values were determined. Structures of the more complicated molecules are in Figure 1.

4-Nitroanisole (4NAN). In addition to the $\log P$ values in the water-heptane (1.37), water-dichloromethane (3.13), water-trichloromethane (3.09), water-toluene (2.64), and water-octanol (2.01) systems [8] there are also available values in the water-isooctane (1.32), water-trichloromethane (3.18), water-PGDP (2.40) and water-octanol (2.03) systems [22]. HPLC retention data for which we have equations, Table 1, have been published [23], and a GLC retention is known [24]. All these yielded 19 simultaneous equations. We took E as 0.89 [8] and V as 1.0902 [9,11,19,20]. We were left as unknowns S , A , B , L , and $\log K_w$. With the descriptors given in Table 2, the 19 equations led to a standard deviation of only 0.055 log units as between observed and calculated dependent variables. The values of the descriptors in Table 2 are quite close to those obtained before [8] but now include L and the very important descriptor $\log K_w$. The observed and calculated dependent variables are given in Table 3.

2,4,6-Trinitrotoluene (TNT). We have the five $\log P$ values of Di Toro et al. [8], there are a few solubilities in number of solvents [25,26] and solubilities in water-methanol mixtures [27] that can be converted into values of $\log P$ through Eq. 3, with $\log S_w = -3.31$ [6]. HPLC retention data

Table 1. Coefficients in Eq. (1) and Eq. (2) for partitions from water and from the gas phase to various solvents, and for HPLC and GLC retention data.

	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>
Solvent, log P, Eq. (1)						
Hexane, wd	0.333	0.560	−1.710	−3.578	−4.939	4.463
Heptane, wd	0.297	0.634	−1.755	−3.571	−4.946	4.488
Hexadecane, wd	0.087	0.667	−1.617	−3.587	−4.869	4.433
Isooctane, wd	0.318	0.555	−1.737	−3.677	−4.864	4.417
Cyclohexane, wd	0.159	0.784	−1.678	−3.740	−4.929	4.577
Trichloromethane, wd	0.191	0.105	−0.403	−3.112	−3.514	4.395
Tetrachloromethane, wd	0.199	0.523	−1.159	−3.560	−4.594	4.618
1,2-Dichloroethane, wd	0.183	0.294	−0.134	−2.801	−4.291	4.180
Carbon disulfide, wd	0.047	0.686	−0.943	−3.603	−5.818	4.921
Benzene, wd	0.142	0.464	−0.588	−3.099	−4.625	4.491
Toluene, wd	0.143	0.527	−0.720	−3.010	−4.824	4.545
Dibutylether, wd	0.203	0.369	−0.954	−1.488	−5.426	4.508
PGDP, w ^a	0.093	0.362	−0.588	−1.162	−4.953	4.232
Diethylether, d	0.350	0.358	−0.820	−0.588	−4.956	4.350
1,4-Dioxane, d	0.098	0.350	−0.083	−0.556	−4.826	4.172
Tetrahydrofuran, d	0.207	0.372	−0.392	−0.236	−4.934	4.447
Methyl acetate, d	0.351	0.223	−0.150	−1.035	−4.527	3.972
Ethyl acetate, d	0.328	0.369	−0.446	−0.700	−4.904	4.150
Butyl acetate, d	0.248	0.356	−0.501	−0.867	−4.973	4.281
Propanone, d	0.313	0.312	−0.121	−0.608	−4.753	3.942
Acetonitrile, d	0.413	0.077	0.326	−1.566	−4.391	3.364
Dimethylsulfoxide, d	−0.194	0.327	0.791	1.260	−4.540	3.361
Formamide, d	−0.171	0.070	0.308	0.589	−3.152	2.432
Dimethylformamide, d	−0.305	−0.058	0.343	0.358	−4.865	4.486
N-Methylpyrrolidinone, d	0.147	0.532	0.225	0.840	−4.794	3.674
Pyridine, d	−0.046	0.298	0.000	0.558	−4.504	4.292
Methanol, d	0.276	0.334	−0.714	0.243	−3.320	3.549
Ethanol, d	0.222	0.471	−1.035	0.326	−3.596	3.857
Propan-1-ol, d	0.148	0.436	−1.098	0.389	−3.893	4.036
Propan-2-ol, d	0.102	0.315	−1.020	0.532	−3.865	4.023
Butan-1-ol, d	0.152	0.438	−1.177	0.096	−3.919	4.122
Butan-2-ol, d	0.194	0.383	−0.956	0.134	−3.606	3.829
2-Methylpropan-1-ol, d	0.161	0.310	−1.069	0.183	−3.774	4.040
2-Methylpropan-2-ol, d	0.211	0.171	−0.947	0.331	−4.085	4.109
Pentan-1-ol, d	0.150	0.536	−1.229	0.141	−3.864	4.077
Hexan-1-ol, d	0.115	0.492	−1.164	0.054	−3.978	4.131
Heptan-1-ol, d	0.035	0.398	−1.063	0.002	−4.342	4.317
Octan-1-ol, d	−0.034	0.489	−1.044	−0.024	−4.235	4.218
Decan-1-ol, d	−0.058	0.616	−1.319	0.026	−4.153	4.279
Ethylene glycol, d	−0.243	0.695	−0.670	0.726	−2.399	2.670
Octan-1-ol, w	0.088	0.562	−1.054	0.034	−3.460	3.814
96 % vol Ethanol-water	0.238	0.353	−0.833	0.297	−3.533	3.724
95 % vol Ethanol-water	0.239	0.328	−0.795	0.294	−3.514	3.697
90 % vol Ethanol-water	0.243	0.213	−0.575	0.262	−3.450	3.545
80 % vol Ethanol-water	0.172	0.175	−0.465	0.260	−3.212	3.323
70 % vol Ethanol-water	0.063	0.085	−0.368	0.311	−2.936	3.102
60 % vol Ethanol-water	−0.040	0.138	−0.335	0.293	−2.675	2.812
50 % vol Ethanol-water	−0.142	0.124	−0.252	0.251	−2.275	2.415
40 % vol Ethanol-water	−0.221	0.131	−0.159	0.171	−1.809	1.918
30 % vol Ethanol-water	−0.269	0.107	−0.098	0.133	−1.316	1.414
20 % vol Ethanol-water	−0.252	0.042	−0.040	0.096	−0.823	0.916
10 % vol Ethanol-water	−0.173	−0.023	−0.001	0.065	−0.372	0.454
Gas to water	−0.994	0.577	2.549	3.813	4.841	−0.869
HPLC retentions, log k'						
HPLC-Arylether phase [23]	−0.936	0.476	−0.445	−0.458	−1.349	2.187
HPLC-Octadecyl phase [23]	−0.396	−0.112	−0.344	−0.344	−1.957	2.514
HPLC-Phenyl phase [23]	−0.397	−0.034	−0.356	−0.158	−0.702	1.670

Table 1. continued

	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>
HPLC-Acclaim E2 [32]	0.080	0.876	−0.205	−0.559	−2.077	1.085
HPLC-40-Cyanopropyl [31]	0.320	−0.072	0.029	−0.008	−0.380	0.523
HPLC-30-Cyanopropyl [31]	0.390	−0.382	0.126	0.068	−0.565	0.804
HPLC-20-Cyanopropyl [31]	0.449	−0.576	0.169	0.115	−0.791	1.060
HPLC-15-Cyanopropyl [31]	0.499	−0.717	0.192	0.154	−0.895	1.217
HPLC-UltrasepESphen [39]	1.082	0.135	−0.197	−0.196	−0.851	0.848
HPLC-Octadecyl phase [30]	0.401	0.102	−0.112	−0.436	−1.540	1.193
HPLC-RP18 [28]	−0.044	−0.240	−0.425	−0.388	−0.965	1.711
HPLC-OD2 [28]	−0.309	−0.349	−0.320	−0.290	−1.073	1.853
HPLC-INAPH [28]	−0.560	−0.533	0.201	−0.701	−0.739	1.765
HPLC-pMOB [28]	−0.653	−0.209	0.015	−0.516	−0.897	1.597
HPLC-CN [28]	−0.532	−0.143	0.123	−0.167	−0.166	0.610
HPLC-mCF3B [28]	−0.488	−0.850	0.169	−0.573	−0.729	1.734
HPLC-5-Mind [28]	−0.477	−0.172	0.107	−0.237	−0.150	0.432
Solvent, log <i>K</i> , Eq. (2)	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>
Hexane, wd	0.320	0.000	0.000	0.000	0.000	0.945
Heptane, wd	0.284	0.000	0.000	0.000	0.000	0.950
Hexadecane, wd	0.000	0.000	0.000	0.000	0.000	1.000
Isooctane, wd	0.264	−0.230	0.000	0.000	0.000	0.975
Cyclohexane, wd	0.163	−0.110	0.000	0.000	0.000	1.013
Trichloromethane, wd	0.157	−0.560	1.259	0.374	1.333	0.976
Tetrachloromethane, wd	0.217	−0.435	0.554	0.000	0.000	1.069
1,2-Dichloroethane, wd	0.017	−0.337	1.600	0.774	0.637	0.921
Carbon disulfide, wd	0.101	0.251	0.177	0.027	0.095	1.068
Benzene, wd	0.107	−0.313	1.053	0.457	0.169	1.020
Toluene, wd	0.121	−0.222	0.938	0.467	0.099	1.012
Dibutylether, wd	0.165	−0.421	0.760	2.102	−0.664	1.002
PGDP, w	−0.020	−0.270	1.048	2.314	0.000	0.947
Diethylether, d	0.288	−0.379	0.904	2.937	0.000	0.963
1,4-Dioxane, d	−0.034	−0.354	1.674	3.021	0.000	0.919
Tetrahydrofuran, d	0.189	−0.347	1.238	3.289	0.000	0.982
Methyl acetate, d	0.134	−0.477	1.749	2.678	0.000	0.876
Ethyl acetate, d	0.182	−0.352	1.316	2.891	0.000	0.916
Butyl acetate, d	0.147	−0.414	1.212	2.623	0.000	0.954
Propanone, d	0.217	−0.387	1.733	3.060	0.000	0.866
Acetonitrile, d	−0.007	−0.595	2.461	2.085	0.418	0.738
Dimethylsulfoxide, d	−0.556	−0.223	2.903	5.037	0.000	0.719
Formamide, d	−0.800	0.310	2.292	4.130	1.933	0.442
Dimethylformamide, d	−0.391	−0.869	2.107	3.774	0.000	1.011
N-Methylpyrrolidinone, d	−0.128	−0.029	2.217	4.429	0.000	0.777
Pyridine, d	−0.123	−0.588	1.991	4.363	0.000	0.942
Methanol, d	−0.039	−0.338	1.317	3.826	1.396	0.773
Ethanol, d	0.017	−0.232	0.867	3.894	1.192	0.846
Propan-1-ol, d	−0.042	−0.246	0.749	3.888	1.076	0.874
Propan-2-ol, d	−0.048	−0.324	0.713	4.036	1.055	0.884
Butan-1-ol	−0.004	−0.285	0.768	3.705	0.879	0.890
Butan-2-ol, d	−0.017	−0.376	0.852	3.740	1.161	0.867
2-Methylpropan-1-ol, d	0.012	−0.407	0.670	3.645	1.283	0.895
2-Methylpropan-2-ol, d	0.053	−0.443	0.699	4.026	0.882	0.907
Pentan-1-ol, d	−0.002	−0.161	0.535	3.778	0.960	0.900
Hexan-1-ol, d	−0.014	−0.205	0.583	3.621	0.891	0.913
Heptan-1-ol, d	−0.056	−0.216	0.554	3.596	0.803	0.933
Octan-1-ol, d	−0.147	−0.214	0.561	3.507	0.749	0.943
Decan-1-ol, d	−0.139	−0.090	0.356	3.547	0.727	0.958
Ethylene glycol, d	−0.887	0.132	1.657	4.457	2.355	0.565
Octan-1-ol, w	−0.222	0.088	0.701	3.473	1.477	0.851
96 % vol Ethanol-water	−0.032	−0.181	0.980	3.940	1.379	0.802
95 % vol Ethanol-water	−0.040	−0.200	1.024	3.950	1.400	0.795
90 % vol Ethanol-water	−0.084	−0.280	1.180	3.959	1.474	0.757

Table 1. continued

	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>
80 % vol Ethanol-water	−0.253	−0.278	1.400	4.000	1.775	0.715
70 % vol Ethanol-water	−0.438	−0.255	1.548	4.040	2.074	0.659
60 % vol Ethanol-water	−0.631	−0.186	1.646	4.054	2.355	0.584
50 % vol Ethanol-water	−0.851	−0.063	1.806	4.050	2.745	0.479
40 % vol Ethanol-water	−1.074	0.075	2.076	4.020	3.196	0.347
30 % vol Ethanol-water	−1.258	0.194	2.300	4.000	3.713	0.206
20 % vol Ethanol-water	−1.364	0.383	2.385	3.950	4.280	0.065
10 % vol Ethanol-water	−1.447	0.446	2.536	3.905	4.750	−0.052
Gas to water	−1.271	0.822	2.743	3.904	4.814	−0.213
GLC Retention index I/1000						
a-140 [29]	0.075	−0.196	0.372	−0.264	0.000	0.198
a-170 [29]	0.076	−0.197	0.372	−0.264	0.000	0.198
b-160 [29]	0.076	−0.459	0.638	−0.083	0.000	0.198
c-150 [29]	0.076	−0.096	0.430	−0.389	0.000	0.198
c-170 [29]	0.077	−0.049	0.411	−0.494	0.000	0.198
d-180 [29]	0.075	−0.928	1.402	0.182	0.000	0.198
d-200 [29]	0.078	−0.932	1.426	0.093	0.000	0.198
NIST [24] ^b	0.070	0.012	0.076	0.000	0.000	0.200

^a PGDP is propylene glycol dipelargonate. ^b is National Institute of Standards and Technology.

Table 2. Descriptors for nitro compounds and high-energy compounds; acronyms are given in the text.

Compound	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	<i>V</i>	<i>L</i>	Log Kw
4NAN	0.89	1.33	0.04	0.38	1.0902	5.345	3.96
TNT	1.39	1.76	0.12	0.63	1.3799	7.354	6.54
TNB	1.37	1.90	0.20	0.55	1.2390	7.044	7.06
RDX	1.38	2.35	0.56	0.55	1.2447	7.532	9.50
HMX	1.77	3.50	0.76	1.04	1.6596	10.65	15.47
MXN	1.32	2.59	0.42	0.52	1.1860	7.435	9.47
DNX	1.26	2.40	0.39	0.56	1.1273	6.980	9.08
TNX	1.19	2.19	0.27	0.60	1.0686	6.465	8.29
Tetryl	1.82	1.62	0.46	0.97	1.6539	8.703	9.20
HNS	3.02	1.96	0.36	1.93	2.6082	14.39	14.16
23DNT	1.15	1.66	0.00	0.45	1.2057	6.327	5.04
24DNT	1.15	1.63	0.00	0.44	1.2057	6.162	4.93
25DNT	1.15	1.62	0.00	0.45	1.2057	6.247	4.94
26DNT	1.15	1.55	0.00	0.45	1.2057	6.129	4.76
34DNT	1.15	1.71	0.00	0.43	1.2057	6.405	5.07
35DNT	1.15	1.61	0.00	0.45	1.2057	6.269	4.92
24DNA	1.19	1.96	0.00	0.65	1.2644	6.916	6.74

are available, [23,28] and there is an extensive set of GLC retention data for TNT [29]. From this experimental data, we could construct no less than 49 simultaneous equations from which to derive the descriptors. We took *E* = 1.39 [8] and *V* = 1.3799 as before. The solution of the set of 49 simultaneous equations yielded the descriptors shown in Table 2, with SD = 0.111 log units. Our value for log Kw, 6.54, can be compared to that of Sandler et al. [6] of 6.18 as obtained from the water solubility and vapor pressure of TNT. The experimental and calculated values are in Table 4. We left out two experimental values of log *P* that were quite out of line (see Table 4).

1,3,5-Trinitrobenzene (TNB). Di Toro et al. [8] determined log *P* values in five water-solvent systems and we could find no other values. There are a few solubilities in non-aqueous solvents [25] and an NIST GLC retention index [24]. However, there have been several studies of HPLC [23,28,30–32] retention data, and Caulfield et al. [29] have reported GLC retention data for TNB. We took *E* = 1.37 [8] and *V* = 1.2390 and were able to solve a set of no less than 39 simultaneous equations with an SD of 0.103 log units. The descriptors that we obtained are in Table 2. We included log *Sw* as an additional unknown and obtained a value of −2.81 as compared to known values of −2.89 [33], −2.74 [34], and −2.71 [25]. We left out three of the log *P*

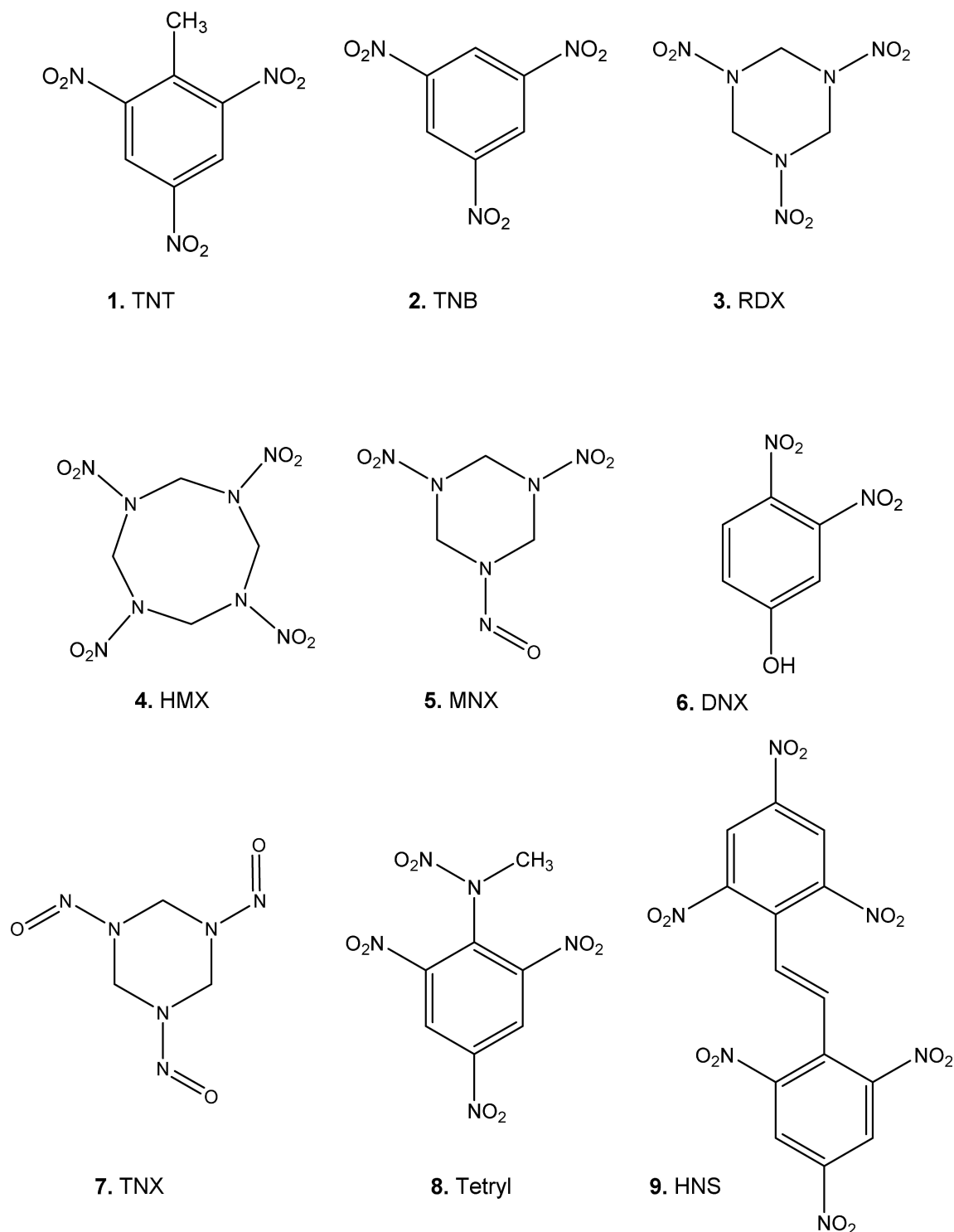


Figure 1. Structures of the more complicated molecules.

values of Di Toro et al. [8] that were considered outliers, as shown in Table 5.

Hexahydro-1,3,5-trinitro-1,3,5-triazaclohexane (RDX). The only water-solvent partition coefficients available are for the systems studied by Di Toro et al. [8]. However, quite

a number of solubilities in non-aqueous solvents have been determined [35–37] and these can be converted into water-(dry)-solvent partition coefficients through $\log S_w = -3.60$ [34]. There is also GLC data [38] and a substantial amount of HPLC retention data [23,31,39] that have been reported.

Table 3. 4-Nitroanisole; calculated and experimental values of the dependent variables, from partitions in water-solvent systems: log **P** the water-solvent partition, and log **K** the gas-solvent partition.

	Calc	Exp
Log P		
Octan-1-ol	2.03	2.03
Dichloromethane	3.20	3.13
Trichloromethane	3.08	3.18
Heptane	1.40	1.37
Isooctane	1.32	1.32
Gas-water/298	3.95	3.96
Toluene	2.66	2.64
PGDP	2.32	2.4
HPLC-Aryl (log <i>k'</i>)	0.75	0.79
HPLC-ODS (log <i>k'</i>)	1.03	0.95
HPLC-Phenyl (log <i>k'</i>)	0.65	0.71
Log K		
Octan-1-ol	6.04	5.99
Dichloromethane	7.17	7.09
Trichloromethane	7.07	7.14
Isooctane	5.27	5.28
Gas-water/298	3.96	3.96
Toluene	6.63	6.6
PGDP	6.29	6.36
NIST/1000	1.25	1.27

Two of the Di Toro et al. [8] partition coefficients were quite out of line when we analyzed the set of simultaneous equations Table 6, but even so, we had 36 simultaneous equations with which to determine descriptors. We took **E** = 1.38 [8] and **V** = 1.2447 and solved the set of simultaneous equations with **SD** = 0.127 log units to yield the descriptors in Table 2.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (Octogen, HMX). Di Toro et al. [8] have determined log **P** values in four water-solvent systems, and there is a reasonable amount of data on solubilities in nonaqueous solvents [40–42]. These can be converted into log **P** values for water to (dry) non-aqueous solvents, taking log **Sw** as –4.82 [43]. Unfortunately, there is no connection at all between the two sets of log **P** values – the first time that we have encountered this difficulty. The best we could do was to use only the log **P** values of Di Toro et al., which when combined with log **Kw**, as in Eq. (4), led to six simultaneous equations. We took **E** = 1.77 [8] and **V** = 1.6596 and solved the set to yield the descriptors in Table 2 with **SD** = 0.016 log units. Although the **SD** is very small, we regard the obtained descriptors as no more than preliminary values.

Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX). The only relevant data we could find were the log **P** values of Di Toro et al. [8] and retention on an HPLC column [39]. We took **E** = 1.32 [8], **V** = 1.1860, and solved the set of nine simultaneous equations to yield the descriptors in Table 2 with **SD** = 0.045 log units.

Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX). Again, we found only the log **P** values of Di Toro et al. [8]

Table 4. 2,4,6-Trinitrotoluene; calculated and experimental values of the dependent variable: log **P** the water-solvent partition, log *k'* the HPLC retention, log **K** the gas-solvent partition, and **I** the GLC retention index.

	Calc	Exp	Ref
Log P			
Octanol	2.10	1.62 ^a	[8] ^a
Dichloromethane	3.16	3.17	[8]
Tetrachloromethane	1.94	2.07	[26]
Hexane	0.72	0.77	[8]
Gas-water/298	6.60	6.54	
Toluene	2.48	3.13 ^a	[8] ^a
Carbon disulfide	2.03	1.85	[26]
Methanol	2.32	2.49	[27]
Ethanol	2.15	2.23	[25]
Diethylether	2.21	2.38	[26]
10% Methanol	0.18	0.23	[27]
20% Methanol	0.40	0.46	[27]
30% Methanol	0.63	0.70	[27]
40% Methanol	0.89	0.93	[27]
50% Methanol	1.17	1.16	[27]
60% Methanol	1.46	1.38	[27]
70% Methanol	1.74	1.60	[27]
80% Methanol	2.00	1.83	[27]
90% methanol	2.20	2.10	[27]
95% Methanol	2.29	2.28	[27]
Log <i>k'</i>			
HPLC-Aryl	1.06	0.98	[23]
HPLC RP18	0.58	0.46	[28]
HPLC OD2	0.49	0.44	[28]
HPLC CN	0.20	0.25	[28]
HPLC mCF3B	0.49	0.60	[28]
HPLC JMWd	–0.06	0.11	[28]
Log K	Calc	Exp	
Dichloromethane	9.71	9.71	
Tetrachloromethane	8.45	8.61	
Hexane	7.27	7.31	
Gas-water/298	6.63	6.54	
Carbon disulfide	8.68	8.39	
Methanol	8.83	9.03	
Ethanol	8.66	8.77	
Diethylether	8.79	8.92	
10% Methanol	6.68	6.77	
20% Methanol	6.89	7.00	
30% Methanol	7.13	7.23	
40% Methanol	7.39	7.47	
50% Methanol	7.68	7.69	
60% Methanol	8.00	7.92	
70% Methanol	8.29	8.14	
80% Methanol	8.55	8.37	
90% Methanol	8.76	8.64	
95% Methanol	8.84	8.82	
GLC Retention index, I /1000			
a140	1.91	1.89	[29]
a170	1.95	1.91	[29]
b160	2.01	2.06	[29]
c150	2.15	2.12	[29]
c160	2.19	2.13	[29]
d180	2.71	2.80	[29]
d200	2.74	2.82	[29]

^a Not used in the calculation.

Table 5. 1,3,5-Trinitrobenzene; calculated and experimental values of the dependent variable: log *P* the water-solvent partition, log *k'* the HPLC retention, log *K* the gas-solvent partition, and *I* the GLC retention index.

	Calc	Exp	Ref
Log <i>P</i>			
Octanol	1.68	1.11 ^a	[8] ^a
Dichloromethane	2.54	2.01 ^a	[8] ^a
Trichloromethane	2.40	2.49	[25]
Tetrachloromethane	1.12	1.18	[25]
Hexane	-0.13	0.01	[8]
Gas -water	7.08	7.07	
Toluene	1.82	2.61 ^a	[8] ^a
CS ₂	1.30	1.10	[25]
Methanol	1.99	2.08	[25]
Ethanol	1.76	1.78	[25]
Ethanol	1.76	1.75	[25]
Diethyl ether	1.81	1.65	[25]
Pyridine	3.39	3.59	[25]
Log <i>k'</i>			
HPLC	0.86	0.88	[30]
HPLC	0.86	0.75	[30]
HPLC-aryl	0.74	0.84	[23]
HPLC RP18	0.32	0.32	[28]
HPLC OD2	0.24	0.23	[28]
HPLC CN	0.13	0.15	[28]
HPLC mCF3B	0.29	0.40	[28]
HPLC-Kaiser 40	0.71	0.66	[31]
HPLC Kaiser 30	0.81	0.72	[31]
HPLC Kaiser 20	0.88	0.76	[31]
HPLC Kaiser 15	0.93	0.79	[31]
HPLC	0.97	0.84	[32]
Log <i>K</i>			
Trichloromethane	9.48	9.56	
Tetrachloromethane	8.21	8.25	
Gas-water	7.08	7.07	
CS ₂	8.36	8.17	
Methanol	9.06	9.15	
Ethanol	8.82	8.85	
Diethylether	8.919	8.724	
Pyridine	10.572	10.656	
GLC Retention index, <i>I</i>/1000			
NIST	1.640	1.837	[24]
a140	1.909	1.882	[29]
a170	1.939	1.896	[29]
b160	2.052	2.094	[29]
c150	2.158	2.13	[29]
c170	2.193	2.142	[29]
d180	2.869	2.859	[29]
d200	2.908	2.884	[29]

^a Not used in the calculation

that we could use. The value of 0.59 for the water-trichloromethane system was a considerable outlier. If this was omitted we had 10 simultaneous equations that we solved with *SD* = 0.050 log units to yield the descriptors in Table 2. We fixed *E* = 1.26 [8] and *V* = 1.1273.

Table 6. RDX; calculated and experimental values of the dependent variable: log *P* the water-solvent partition, log *k'* the HPLC retention, log *K* the gas-solvent partition, and GLC retention data.

	Calc	Exp	Ref
Log <i>P</i>			
Octanol	1.26	0.87 ^a	[8] ^a
Dichloromethane	1.44	1.27	[8]
Trichloromethane	1.18	0.71 ^a	[8] ^a
Hexane	-2.08	-2.10	[8]
Gas-water	9.52	9.51	
Toluene	0.54	0.74	[8]
Ethanol	1.45	1.40	[35]
Propanol	1.32	1.31	[35]
Butanol	1.24	1.10	[35]
Propan-2-ol	1.26	1.19	[35]
Isobutanol	1.04	1.01	[35]
Propanone	2.42	2.22	[37]
Dimethylformamide	3.54	3.80	[36]
N-Methylpyrrolidinone	3.83	3.87	[36]
Log <i>k'</i>			
HPLC	1.28	1.39	[23]
HPLC-Kaiser-40	0.73	0.82	[31]
HPLC-Kaiser-30	0.89	0.92	[31]
HPLC-Kaiser 20	1.00	0.99	[31]
HPLC-Kaiser 15	1.07	1.02	[31]
Log <i>K</i>			
Dichloromethane	10.90	10.78	
Hexane	7.44	7.41	
Gas-water	9.55	9.51	
Toluene	10.01	10.24	
Ethanol	10.96	10.91	
Propan-1-ol	10.74	10.82	
Butan-1-ol	10.68	10.61	
Propan-2-ol	10.69	10.70	
Isobutanol	10.49	10.52	
Propanone	11.91	11.73	
Dimethylformamide	13.10	13.30	
N-Methylpyrrolidinone	13.39	13.37	
GLC retention data			
GLC NIST	1.77	1.91	[24]
GLC DB-126	0.97	0.75	[38]
GLC DB-76	1.07	0.84	[38]
GLC DB-77	1.14	0.95	[38]
RTX-200-40	1.51	1.47	[38]
RTX-200-122	0.37	0.46	[38]
RTX-200-225	1.25	1.14	[38]

^a Not used in the calculation

Hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX). We had only the log *P* values of Di Toro et al. [8]; that for the water-trichloromethane system was again out of line and so we were left again with 10 simultaneous equations. We took *E* = 1.19 [8], *V* = 1.0686 and solved the set of equations with *SD* = 0.104 log units. The obtained descriptors are in Table 2.

There are a number of other nitro or high energy compounds that were not examined by Di Toro et al. [8], and for which there is enough data available to construct sets of simultaneous equations in order to obtain the descriptors. We consider these as follows.

N-Methyl-N-2,4,6-tetranitroaniline (Tetryl). We could find no experimental log *P* values for tetryl but solubilities in several non-aqueous solvents are available [44]. These can be converted into water – dry solvent partition coefficients through Eq. (3), taking log *Sw* as –3.56 [44,45]. There is also data on HPLC [30–32] and GLC retentions [38], and we were able to construct 20 simultaneous equations. We took *E* = 1.82 [11] and *V* = 1.6539, and solved the equations with *SD* = 0.227 log units to yield the descriptors in Table 2.

Hexanitrostilbene (HNS). Reports on the solubility of HNS are available [46,47], but the experimental data are inconsistent, and so we used only the solubilities recorded by Chen et al. [47]. There is just enough data to obtain the descriptors listed in Table 2; we took *E* = 3.02, estimated by addition of fragments, and *V* = 2.6082. *N* = 10 and *SD* = 0.150 log units.

Dinitrotoluene (DNT). There is considerable data available on HPLC [28] and GLC [29] retention data on the six dinitrotoluenes, as well as log *P* values for the water-octan-1-ol system [22]. We took *E* = 1.15 [11,20] and *V* = 1.2057, and then obtained the (revised) descriptors as shown in Table 2. For 23DNT the number of simultaneous equations *N* = 11 and *SD* = 0.041, for 24DNT *N* = 17 and *SD* = 0.063, for 25DNT *N* = 4 and *SD* = 0.015, for 26DNT *N* = 18 and *SD* = 0.029, for 34DNT *N* = 18 and *SD* = 0.032 and for 35DNT *N* = 11 and *SD* = 0.018 log units.

2,4-Dinitroanisole (24DNA). There is just enough data on solubilities of 24DNA in non-aqueous solvents [25], coupled with a value of log *P* = 1.61 in the water-octan-1-ol system [48] to obtain provisional values of descriptors. We took log *Sw* = –2.86 [48] to convert solubilities into log *P* values, *E* = 1.19 [21] and *V* = 1.2644, and obtained the descriptors in Table 2 from seven simultaneous equations with *SD* = 0.048 log units.

4 Discussion

We show that it is possible to use a variety of physicochemical processes in order to obtain descriptors for nitro and high energy compounds. As well as water-solvent partition coefficients, used by Di Toro et al. [8], we also incorporated solubilities in non-aqueous solvents and HPLC and GLC retention data, thus leading to a considerable number of simultaneous equations to solve for the descriptors. The number of equations that we could construct is enhanced by our method of analysis, as compared to the method of Di Toro et al. [8]. The latter start with a number of water-solvent partition coefficients, usually five. Then they have five simultaneous equations with which to obtain

the descriptors *S*, *A*, and *B* (*E* and *V* being fixed prior to the analysis). On our method, we convert the five values of log *P* into five corresponding values of log *Ks* through Eq. (4) by taking log *Kw* as another unknown parameter to be determined. We also have two extra equations in log *Kw*, see Table 2, thus leading to a total of twelve simultaneous equations from which we can obtain not only *S*, *A*, and *B*, but also *L* and the important descriptor log *Kw*. There will inevitably be compounds for which there is no experimental data or only limited experimental data that can be used to obtain the required descriptors. However, descriptors can be calculated just from structure [11,20]. Either an entire set of descriptors can be obtained in this way, or the calculated descriptors can be combined with results from the limited experimental data.

Once the descriptors for a given compound are obtained, see Table 2, they can be used to estimate a very large number of log *P* and log *Ks* values, using the equation coefficients in Table 1 and elsewhere [13,18]. If a value of log *Sw* is available, then the estimated values of log *P* can be converted into solubilities, as log *Ss* through Eq. 3. Numerous other properties can also be estimated, including vapor pressure [49] enthalpies of vaporization [50] enthalpies of sublimation [51] and heat capacities [52] at 298 K, as well as properties of environmental interest [53]. All these estimations can be calculated by simple arithmetic. The vapor pressures and enthalpies of sublimation are of special interest partly because of the difficulty in obtaining reliable experimental data [54,55]. For example, reported values [55] for ΔH_{sub} for TNT vary between 81000 and 144000 J mol^{–1}.

The equations for the vapor pressure of liquids (log *VPvap*/MPa) and solids (log *VPsub*/MPa), the enthalpy of vaporization (ΔH_{vap} /J mol^{–1}), the enthalpy of sublimation (ΔH_{sub} /J mol^{–1}), the heat capacity of vaporization ($\Delta_{\text{vap}}C_p$ /JK^{–1}mol^{–1}) and the heat capacity of sublimation ($\Delta_{\text{sub}}C_p$ /JK^{–1}mol^{–1}) 298.15 K are given as Eq. (5) to Eq. (10), for compounds that are not aliphatic diols or aliphatic amines.

$$\text{Log VPvap/MPa} = 1.588 - 0.759 E - 1.190 S - 1.138 A - 3.382 V - 0.456 S^*S - 3.412 A^*B \quad (5)$$

$$\text{Log VPsub/MPa} = 1.875 - 0.596 E - 2.977 S - 0.285 A + 0.252 B - 3.037 V - 5.611 A^*B - 0.136 V^*V \quad (6)$$

$$\Delta H_{\text{vap}}/\text{J mol}^{-1} = -3008 + 5226 E + 18422 S + 8978 A + 1363 B + 34141 V - 2045 S^*S + 75728 A^*B \quad (7)$$

$$\Delta H_{\text{sub}}/\text{J mol}^{-1} = 9960 - 2100 E + 24100 S + 13700 A + 790 B + 38710 V - 1360 S^*S + 36900 A^*B + 1860 V^*V \quad (8)$$

$$\Delta_{\text{vap}}\text{Cp}/\text{JK}^{-1}\text{mol}^{-1} = -13.98 - 9.21\text{E} + 0.15\text{S} \\ -42.07\text{A} - 35.72\text{B} - 33.64\text{V} + 5.42\text{S}^*\text{S} - 9.63\text{A}^*\text{B} \\ -3.75\text{V}^*\text{V} \quad (9)$$

$$\Delta_{\text{sub}}\text{Cp}/\text{JK}^{-1}\text{mol}^{-1} = -17.15 + 12.20\text{E} - 16.19\text{S} \\ +14.34\text{A} + 4.26\text{B} - 27.47\text{V} + 6.28\text{S}^*\text{S} - 6.32\text{A}^*\text{B} \\ +3.68\text{V}^*\text{V} \quad (10)$$

It is then straightforward to enter the descriptors we have determined, Table 2, into Eq. (5)–Eq. (10) to calculate the required parameters. It should be noted that the calculated values are outright predictions, because the data in Table 2 have not been used to construct Eq. (5)–Eq. (10). Since experimental values for log $\text{VP}(\text{sub})$ and for $\Delta\text{H}_{\text{sub}}$ vary so much, we used the recent analysis of Östmark et al. [56], see also [57], who have examined literature data and listed preferred values. The experimental and predicted values are in Table 7. We could not find experimental values for some compounds, but we give the predicted values. Considering the possible experimental error, agreement between experimental and predicted values is very good. We give also our predicted values of $\Delta_{\text{vap}}\text{Cp}$ and $\Delta_{\text{sub}}\text{Cp}$ through Eq. (9) and Eq. (10). These quantities are valuable in correcting experimental values of $\Delta\text{H}_{\text{vap}}$ and $\Delta\text{H}_{\text{sub}}$ back to a standard temperature of 298 K. The results in Table 7 illustrate the potential of the use of our descriptors in the prediction of thermodynamic properties.

The problem of inconsistent experimental values that we noted, above, is not confined to vapor pressures and

enthalpies of sublimation. Boddu et al. [48] determined the solubility of 2,4-dinitroanisole in water, log $\text{Sw} = -2.86$, and a reasonable experimental value for log VP/MPa is -8.83 [54]. Now $\text{Kw} = \text{Sw}/\text{Sg}$ where Sg is the molar concentration of the compound in the gas phase. From the value of log VP , log $\text{Cg} = -9.20$ and hence log $\text{Kw} = 6.24$. But Boddu et al. [46] find that log $\text{Kw} = 3.26$, a difference of three log units. Our value of log Kw is 6.74 (Table 2), in reasonable agreement with the value of 6.24 obtained from log Sw and log Sg .

The high energy nitro compounds can be taken up by soils and then transferred to humans through absorption by skin. Not surprisingly, there have been several studies of absorption from soils into human skin, see for example the study by Mark et al. [58]. However, these compounds can also be taken up by stagnant water and then transferred to humans by contact of the water with skin. This is another potential environmental hazard but has received almost no attention. If a compound is present as a dilute solution in water, the quantity of the compound that will be taken up by human skin is given [59] by Eqn. (11), where Q is the accumulative amount of compound (mole) permeating through the skin, t is the time of immersion in seconds, As is the area of skin in contact with water in cm^2 , and Cw is the concentration of the compound in water, in mol cm^{-3} .

$$\partial\text{Q}/\partial t = \text{Kp}^*\text{As}^*\text{Cw} \quad (11)$$

Values of t , As and Cw will be known, but in order to obtain Q , it is necessary to know the skin permeability, Kp , at 310.15 K. This is unavailable for the compounds in Ta-

Table 7. Experimental and predicted values of vapor pressure of sublimation, and enthalpies of sublimation; predicted values of heat capacities of vaporization and sublimation at 298.15 K.

Compound	Log $\text{VP}_{\text{sub}}/\text{MPa}$		$\Delta\text{H}_{\text{sub}}/\text{J mol}^{-1}$		$\Delta_{\text{vap}}\text{Cp}$	$\Delta_{\text{sub}}\text{Cp}$
	Expt [56]	Pred	Expt [56]	Pred	Pred	Pred
4-Nitroanisole		−6.09		83500	−68.9	−40.2
TNT	−9.14	−8.95	114100	107000	−91.6	−36.2
TNB		−9.11	107300	105900	−83.3	−32.4
RDX	−12.34	−11.69	127100	126300	−90.3	−23.7
HMX	−18.38	−19.41	174700	182500	−136.0	−63.8
MXN		−11.64		122900	−98.9	−64.3
DNX		−10.82		116800	−96.0	−60.0
TNX		−9.60		107100	−91.1	−58.8
Tetryl	−12.08	−11.82	133900	133600	−128.9	−44.6
HNS	−21.21	−18.13	179600	190300	−200.2	−57.2
HNS	−16.97 [57]	−18.13	151100 [57]	190300	−200.2	−57.2
2,3-DNT		−7.50		93500	−83.8	−64.0
2,4-DNT	−7.46	−7.42	94000	92900	−83.3	−63.5
2,5-DNT		−7.39		92700	−83.7	−63.3
2,6-DNT	−7.08	−7.18	100900	91400	−83.6	−62.0
3,4-DNT		−7.66		94500	−83.2	−65.0
3,5-DNT		−7.36		92600	−83.7	−63.1
2,4-Dinitroanisole [54]	−8.82	−8.57	248000	101900	−93.9	−69.9
2,4-Dinitroanisole [55]	−9.46	−8.57	124000	101900	−93.9	−69.9

ble 7 but can be predicted through Eq. (12) [60], for compounds unionized in water.

$$\text{Log Kp (cm s}^{-1}\text{)} = -5.420 - 0.102 \text{ E} - 0.457 \text{ S} \\ - 0.324 \text{ A} - 2.680 \text{ B} + 2.066 \text{ V} \quad (12)$$

It would be useful if we had one or two experimental values of log **Kp** for the compounds in Table 2, with which to compare predictions, but we could find no values of log **Kp** at all. The nearest compound to those in Table 2 for which there is an experimental value of log **Kp** is 4-nitrotoluene, with an experimental value of -4.30 [61] as compared to a predicted value of -4.63 . The predicted log **Kp** values for all the compounds in Table 2 are listed in Table 8. HMX has a decidedly lower skin permeability than the other nitro compounds, but otherwise, there is little that is exceptional.

The values of the descriptors are of some interest. The most striking finding is that the cyclic high-energy compounds all have substantial values of the **A**-descriptor, even though they have no 'active' hydrogen atoms. Thus HMX has **A** = 0.76 but the only hydrogen atoms are in the group $\text{N-CH}_2\text{-N}$ and would not be expected to have any substantial hydrogen bond acidity, see Figure 1. We suggest that the presence of the NO_2 groups in the high-energy compounds leads to electron-deficient ring systems that acts as Lewis acids. Compounds with an aliphatic ring system tend to have larger values of **A** than compounds with aromatic ring systems (TNT, TNB, and HNS). Our equations, Eq. 1 and Eq. 2 have no specific descriptor for Lewis acidity and so our hydrogen bond descriptor, **A**, encodes Lewis acidity as well. There is precedent for this behaviour, sulfur dioxide has **A** = 0.28, and bromine has **A** = 0.18. Whatever the mechanism that gives rise to the large **A**-values, it

seems that high energy compounds are characterized by a large **A**-value, something that has not previously been pointed out.

5 Conclusions

We have shown that our methods used previously to obtain properties or 'descriptors' of molecules, can equally well be applied to a set of 'high energy' compounds. The descriptors can then be combined with equations that we have already constructed to yield predictions of a wide range of properties of 'high energy' compounds. These predicted properties include thermodynamic properties such as vapor pressure, enthalpies of vaporization, enthalpies of sublimation, and heat capacities of vaporization and sublimation, as well as important environmental properties such as skin permeation. Many of these properties are difficult to determine by experiment and so predictions are of considerable value.

The determined descriptors of the 'high energy' compounds include those that relate to acidity and basicity. We show, for the first time, that 'high energy' compounds possess substantial acidity possibly through electron-deficient ring systems.

Funding

This research received no grants from any funding agencies in the public, commercial, or not-for-profit sectors.

Data Availability Statement

The data used in this work were all taken from the literature and are available from the open literature.

Table 8. Predicted values of skin permeation, as log **Kp** in cm s^{-1} at 310.15 K, through Eq. (12).

Compound	Log Kp
4-Nitroanisole	−4.90
TNT	−5.24
TNB	−5.41
RDX	−5.72
HMX	−6.80
MXN	−5.82
DNX	−5.94
TNX	−6.03
Tetryl	−5.68
HNS	−6.52
2,3-DNT	−5.01
2,4-DNT	−4.97
2,5-DNT	−4.99
2,6-DNT	−4.96
3,4-DNT	−4.98
3,5-DNT	−4.99
2,4-DNA	−5.57

References

- [1] M. A. Suntsova, O. V. Dorofeeva, Prediction of enthalpies of sublimation of high-energy energetic compounds: modified Polizer method, *J. Mol. Graphics Modell.* **2017**, *72*, 220–228.
- [2] S. Alnemrat, J. P. Hooper, Predicting temperature-dependent solid vapor pressures of explosives and related compounds using a quantum mechanical continuum solvation model, *J. Phys. Chem. A* **2013**, *117*, 2035–2043.
- [3] M. Qasim, Y. Kholod, L. Gorb, D. Magers, P. Honea, J. Leszczynski, Application of quantum-chemical approximations to environmental problems: prediction of physical and chemical properties of TNT and related species, *Chemosphere* **2007**, *69*, 1144–1150.
- [4] R. K. Toghiani, H. Toghiani, S. W. Maloney, V. M. Boddu, Prediction of physicochemical properties of energetic materials, *Fluid Phase Equilib.* **2008**, *264*, 86–92.

- [5] A. Ahmed, S. I. Sandler, Physicochemical properties of hazardous energetic compounds from molecular simulation, *J. Chem. Theory Comput.* **2013**, *9*, 2389–2397.
- [6] A. Ahmed, S. I. Sandler, Hydration free energies of multifunctional nitroaromatic compounds, *J. Chem. Theory Comput.* **2013**, *9*, 2774–2785.
- [7] Y. Liang, R. Xiong, S. I. Sandler, D. M. Di Toro, Quantum chemically estimated Abraham solute parameters using multiple solvent-water partition coefficients and molecular polarizability, *Environ. Sci. Technol.* **2017**, *51*, 9887–9898.
- [8] Y. Liang, D. T. F. Kuo, H. E. Allen, D. M. Di Toro, Experimental determination of solvent-water partition coefficients and Abraham parameters for munition constituents, *Chemosphere* **2016**, *161*, 429–437.
- [9] M. H. Abraham, Scales of hydrogen bonding: their construction and application to physicochemical and biochemical processes, *Chem. Soc. Rev.* **1993**, *22*, 73–83.
- [10] E. D. Clarke, L. Mallon, The Determination of Abraham descriptors and their Application to Crop Protection Research, in *Modern Methods in Crop Protection Research* (Eds.: P. Jeschke, W. Krämer, U. Schirmer, M. Witschel), Wiley-VCH Verlag GmbH & Co., **2012**.
- [11] Absolv. ACD Advanced Chemistry Development, 110 Yonge Street, 14th Floor, Toronto, Ontario, M5C 1T4, Canada.
- [12] M. H. Abraham, W. E. Acree Jr., Solvation descriptors for zwitterionics-aminoacids; estimation of their water-solvent partition coefficients, solubilities and hydrogen-bond acidity and hydrogen-bond basicity, *ACS Omega* **2019**, *4*, 2883–2892.
- [13] R. Fischer, M. Jodray, E. Qian, L. Wang, G. Lee, D. Yue, M. Che, Y. Liu, W. E. Acree, Jr., M. H. Abraham, Abraham model correlations for solute transfer into benzyl alcohol from both water and the gas phase, *Phys. Chem. Liq.* **2020**, *58*, 116–126.
- [14] M. H. Abraham, W. E. Acree, Jr., D. Hoekman, A. J. Leo, M. L. Medlin, A new method for the determination of Henry's Law constants (air-water-partition coefficients), *Fluid Phase Equilib.* **2019**, *502*, 112300/1–112300/10.
- [15] M. H. Abraham, A. Ibrahim, A. M. Zissimos, The determination of sets of solute descriptors from chromatographic measurements, *J. Chromatogr. A* **2004**, *1037*, 29–47.
- [16] C. F. Poole, S. N. Atapattu, S. K. Poole, A. K. Bell, Determination of solute descriptors by chromatographic methods, *Anal. Chim. Acta* **2009**, *652*, 32–53.
- [17] C. F. Poole, T. C. Ariyasena, N. Lenca, Estimation of the environmental properties of compounds from chromatographic measurements and the solvation parameter model, *J. Chromatogr. A* **2013**, *1317*, 85–104.
- [18] M. H. Abraham, R. E. Smith, R. Luchtefeld, A. J. Boorem, R. Luo, W. E. Acree Jr., Prediction of solubility of drugs and other compounds in organic solvents, *J. Pharm. Sci.* **2010**, *99*, 1500–1515.
- [19] M. H. Abraham, J. C. McGowan, The use of characteristic volumes to measure cavity terms in reversed-phase liquid chromatography, *Chromatographia* **1987**, *23*, 243–246.
- [20] UFZ-LSER database: S.Endo, T. N. Brown, N. Watanabe, N. Ulrich, G. Bronner, M. H. Abraham, K.-U. Goss: UFZ-LSER database v 3.1 [Internet], Leipzig, Germany, Helmholtz Centre for Environmental Research-UFZ. **2015**. Available from www.ufz.de/lserd.
- [21] ChemSketch. ACD Advanced Chemistry Development, 110 Yonge Street, 14th Floor, Toronto, Ontario, M5C 1T4, Canada.
- [22] BioLoom, BioByte Corp, 201 W. 4th Street, #204 Claremont, CA 91711–4707, USA.
- [23] T. H. Mourey, S. Siggia, Chemically bonded aryl ether phase for the high performance liquid chromatographic separation of aromatic nitro compounds, *Anal. Chem.* **1979**, *51*, 763–767.
- [24] NIST Chemistry Webbook.
- [25] A. Seidell, *Solubilities of organic compounds*, Third Ed., Volume II, Van Nostrand, New York, **1941**.
- [26] C. A. Taylor, W. H. Rinkenbach, The solubility of trinitrotoluene in organic solvents, *J. Amer. Chem. Soc.* **1923**, *45*, 44–59.
- [27] L. Z. Chen, F. R. Zhou, J. L. Wong, Solubilities of 2,4,6-trinitrotoluene in methanol and binary mixtures of methanol + water from 293.15 to 333.15 K, *J. Soln. Chem.* **2014**, *43*, 2163–2169.
- [28] M. Markuszewski, J. D. Krass, T. Hippe, B. Jastorff, R. Kaliszan, Separation of nitroaromatics and their transformation products in the soil around ammunition plants: new high performance liquid chromatographic charge transfer stationary phases, *Chemosphere* **1998**, *37*, 559–575.
- [29] J. A. Caulfield, T. J. Bruno, K. E. Miller, Enthalpy of solution and Kovats retention indices for nitroaromatic compounds using gas chromatography, *J. Chem. Eng. Data* **2009**, *54*, 1814–1822.
- [30] L. Didaoui, U. Lewin-Kretzschmar, A. Touabef, W. Engewald, Computer-assisted optimization in the development of high-performance liquid chromatographic methods for the analysis of some explosives and related compounds, *Chromatographia* **2003**, *57*, S129–S134.
- [31] M. Kaiser, HPLC investigation of explosives and nitroaromatic compounds with a cyanopropyl phase, *Propellants, Explos. Pyrotech.* **1998**, *23*, 309–312.
- [32] M. Gledhill, A. J. Beck, B. Stamer, C. Schlosser, E. P. Achterberg, Quantification of munition compounds in the marine environment by solid-phase extraction – ultra high-performance liquid chromatography with detection by electrospray ionization – mass spectrometry, *Talanta* **2019**, *200*, 366–372.
- [33] E. N. Muratov, V. E. Kuz'min, A. G. Artemenko, N. A. Kovdienko, L. Gorbby, F. Hill, J. Leszczynski, New QSPR equations for prediction of aqueous solubility for military compounds, *Chemosphere* **2010**, *79*, 887–890.
- [34] S. Alnemrat, J. P. Hooper, Predicting solubility of military, homemade, and green explosives in pure and saline water using COSMO-RS, *Propellants, Explos. Pyrotech.* **2014**, *39*, 79–89.
- [35] J. Liu, Q. Yang, J. Song, W. Jiang, F.-S. Li, Effects of particle size and temperature on solubility of RDX, *Chinese J. Energetic Materials* **2015**, *23*, 537–542.
- [36] M. E. Sitzman, S. C. Foti, Solubilities of explosives – dimethylformamide as a general solvent for explosives, *J. Chem. Eng. Data* **1975**, *20*, 53–55.
- [37] S. Damiri, H. R. Pouretedal, H. Panahi, A. Dris, Statistical optimization and selective separation of RDX and HMX explosives by using binary solvent mixtures containing ethyl acetate and water, *Central Eur. J. Energetic Materials* **2017**, *14*, 391–402.
- [38] M. E. Walsh, T. Ranney, Determination of nitroaromatic, nitramine and nitrate ester explosives in water using solid-phase extraction and gas-chromatography-electroncapture detection: comparison with high-performance liquid chromatography, *J. Chromatographic Sci.* **1998**, *36*, 406–416.
- [39] A. Preiss, A. Bauer, H.-M. Berstermann, S. Gerling, R. Haas, A. Lehmann, L. Schmalz, K. Steinbach, Advanced high-performance liquid chromatography method for highly polar nitroaromatic compounds in ground water samples from ammunition waste sites, *J. Chromatogr. A* **2009**, *1216*, 4968–4975.
- [40] B. Singh, L. K. Chaturvedi, C. M. P. Kujur, P. S. Bhatia, P. N. Gadhihar, Solubility of cyclotetramethylenetetranitramine (HMX) in organic solvents, *Indian J. Technol.* **1976**, *14*, 676–677.
- [41] K. J. Kim, H. S. Kim, J. S. Sim, Solubilities of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in γ -butyrolactone + water, dimethylsulfoxide + water, and N-methylpyrrolidone + water, *J. Chem. Eng. Data* **2013**, *58*, 2410–2413.

- [42] L. Wang, D. Chen, Y. Yu, H. Li, Solubility of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetracine in 12 pure organic solvents, *J. Chem. Eng. Data* **2020**, *65*, 2098–2108.
- [43] J. C. Lynch, K. F. Myers, J. M. Brannon, J. J. Delfino, Effects of pH and temperature on the aqueous solubility and dissolution rate of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), *J. Chem. Eng. Data* **2001**, *46*, 1549–1555.
- [44] C. A. Taylor, W. H. Rinkenbach, The solubility of trinitrophenylmethyl-nitramine (teteryl) in organic solvents, *J. Am. Chem. Soc.* **1923**, *45*, 104–107.
- [45] Y. A. Kholod, E. N. Muratov, L. G. Gorb, F. C. Hill, A. G. Artemenko, V. E. Kuz'min, M. Qasim, J. Leszczynski, Application of quantum chemical approximations to environmental problems: prediction of water solubility for nitrocompounds, *Environ. Sci. Technol.* **2009**, *43*, 9208–9215.
- [46] D. L. Williams, K. D. Kuklenz, A determination of the Hansen solubility parameters of hexanitrostilbene (HNS), *Propellants, Explos. Pyrotech.* **2009**, *34*, 45 2–457.
- [47] L. Chen, L. Song, Y. Gao, A. Zhu, D. Cao, Experimental determination of solubilities and super solubilities of 2,2',4,4',6,6'-hexanitrostilbene in different organic solvents. *Chinese J. Chem. Eng.* **2017**, *25*, 809–814.
- [48] V. M. Boddu, K. Abburi, S. W. Maloney, R. Damavarapu, Thermophysical properties of an insensitive munitions compound, 2,4-dinitroanisole, *J. Chem. Eng. Data* **2008**, *53*, 1120–1125.
- [49] M. H. Abraham, W. E. Acree Jr., Estimation of vapor pressures of liquid and solid organic and organometallic compounds at 298.15 K, *Fluid Phase Equilib.* **2020**, *519*, 112595.
- [50] B. Churchill, W. E. Acree Jr., M. H. Abraham, Development of Abraham Model Expressions for Predicting the Standard Molar Enthalpies of Vaporization of Organic Compounds at 298.15 K, *Thermochim. Acta* **2019**, *681*, 178372.
- [51] M. H. Abraham, W. E. Acree Jr., Estimation of enthalpies of sublimation of organic, organometallic and inorganic compounds, *Fluid Phase Equilib.* **2020**, *515*, 112575.
- [52] M. H. Abraham, W. E. Acree Jr., Estimation of heat capacities of gases, liquids, and solids, and heat capacities of vaporization and sublimation of organic chemicals at 298.15 K, *J. Mol. Liq.* **2020**, *317*, 113969.
- [53] S. Endo, K.-U. Goss, Applications of polyparameter linear free energy relationships in environmental chemistry, *Environ. Sci. Technol.* **2014**, *48*, 12477–12491.
- [54] M. F. Cuddy, A. R. Poda, M. A. Chappell, Estimations of vapor pressures by thermogravimetric analysis of the insensitive munitions IMX-101, IMX-104, and individual components, *Propellants, Explos. Pyrotech.* **2014**, *39*, 236–242.
- [55] R. Lui, T. Zhang, Y. Liu, L. Yang, Z. Zhou, Vaporization characteristics of low-melting nitro compounds by isothermal thermogravimetry, *J. Therm. Anal. Calorim.* **2013**, *112*, 1523–1532.
- [56] H. Östmark, S. Wallin, H. G. Ang, Vapor pressure of explosives: a critical review, *Propellants, Explos. Pyrotech.* **2012**, *37*, 12–23.
- [57] J. E. Brady, J. L. Smith, C. E. Hart, J. Oxley, Estimating ambient vapor pressures of low volatility explosives by rising-temperature thermogravimetry, *Propellants, Explos. Pyrotech.* **2012**, *37*, 215–222.
- [58] N. Mark, J. Arthur, K. Dontsova, M. Brusseau, S. Taylor, J. Simunek, Column transport studies of 3-nitro-1,2,4-triazol-5-one (NTO) into soils, *Chemosphere* **2017**, *171*, 427–434.
- [59] G. Lian, L. Chen, L. Han, An evaluation of mathematical methods for predicting skin permeability, *J. Pharm. Sci.* **2008**, *97*, 584–598.
- [60] K. Zhang, M. Chen, G. K. E. Scriba, M. H. Abraham, A. Fahr, X. Liu, Human skin permeation of neutral species and ionic species: extended linear free-energy relationship analyses, *J. Pharm. Sci.* **2012**, *101*, 2034–2044.
- [61] X. R. Xia, R. E. Baynes, N. A. Monteiro-Riviere and J. E. Riviere, An experimentally based approach for predicting skin permeability of chemicals and drugs using a membrane-coated fiber array, *Toxicol. and Applied Pharmacol.* **2007**, *221*, 320–328.

Manuscript received: May 5, 2020

Revised manuscript received: October 4, 2020

Version of record online: December 23, 2020