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Nitrogen-14 nuclear quadrupole resonance study of substituted nitrobenzenes[a)]

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Nitrogen-14 nuclear quadrupole resonance (NQR) spectra of 26 C–nitro compounds are reported and analyzed in the framework of the Townes and Dailey theory. Six different possibilities for the principal axis system of the electric field gradient (efg) tensor at the nitrogen of the NO_2 group are considered. The results lead to the conclusion that the z direction of the principal axes is in the plane of the molecule and perpendicular to the C–N bond, whereas the x direction is along the C–N bond. The variations of the π electron density are in very good agreement with the ideas of classical chemistry. Satisfactory correlations of NQR data with the Hammett σ and σ_R constants have been found. σ_p and σ_R for the cholesteryl group are determined which suggest that the cholesteryl group, $COOC_{27}H_{45}$, is an electron attracting group. The nitrogen-14 quadrupole coupling constant in the solid phase of nitromethane (1695 kHz) is found to be substantially larger than that found in the gaseous phase (1187 kHz) by microwave measurements. This result cannot be explained by invoking the presence of hydrogen bonds in the solid phase of nitromethane.

INTRODUCTION

Nuclear quadrupole resonance (NQR) spectroscopy[1–3] has become increasingly important as a means of determining the electronic structures of molecules in their ground state. In recent years, nitrogen-14 NQR has found wide application in the study of various families of compounds in a variety of bonding configurations. However, the nitrogen-14 NQR spectra in C-nitro compounds eluded detection until quite recently,[4] possibly because of the low coupling constants and long relaxation times involved. C-nitro compounds form an important class of compounds because of the close relationship with various explosives of which 2, 4, 6-trinitrotoluene (T.N.T.) and 1, 3, 5-trinitrobenzene are notable examples. Moreover, the nitro group seems to be an essential functional group for the pharmacological activity of a number of drugs.[5]

The detection of the NQR spectra in nitromethane and nitrobenzene has been reported by the authors in an earlier paper.[4] The work has been extended to a number of substituted nitrobenzenes in an effort to determine the effect of the different substituents on the electron density at the nitrogen of the nitro group. Correlations of the NQR data with the Hammett σ parameters[6] are considered.

EXPERIMENTAL PROCEDURE

Nitrogen-14 NQR spectra were obtained with a pulsed spectrometer operated in the 90°–180°-echo mode.[7] Since most of the experimental details are given elsewhere,[7] only a brief outline will be presented here. The 90° and 180° pulses were of widths about 20 and 40 microseconds, respectively. The interval between the pulses was in the range of 1–3 milliseconds. Both pulses were of the same height: about 3–4 kV peak-to-peak. Echoes were observed using phase detection techniques[7,8] which allow for more accurate measurement of the frequencies than amplitude detection.

All the measurements were made at liquid nitrogen temperature (77 °K) on polycrystalline samples obtained from commercial sources. In several instances the location of weak spectral lines was accomplished with the aid of a signal averager.[9]

EXPERIMENTAL RESULTS

The nitrogen-14 nucleus has a spin of unity. Therefore, in the presence of an electric field gradient (efg), lacking axial symmetry there are three quadrupole energy levels and hence three transition frequencies.[1–3] Let q_{xx}, q_{yy}, and $q_{zz} \equiv q$ be the diagonal components of the efg tensor in the principal axis system chosen such that

$$|q_{zz}| \geq |q_{yy}| \geq |q_{xx}| \ .$$

Then the three transition frequencies are given by[1–3]

$$\nu_{\pm} = (3/4)e^2 qQ(1 \pm \eta/3) \ , \tag{1}$$

and

$$\nu_d = \nu_+ - \nu_- \ , \tag{2}$$

where eQ is the quadrupole moment of the nucleus, e^2qQ is called the coupling constant, and η is the asymmetry parameter defined as

$$\eta = (q_{xx} - q_{yy})/q_{zz} \ . \tag{3}$$

The asymmetry parameter η is clearly a measure of the departure of the efg from axial symmetry.

Table I lists the frequencies and related parameters of the NQR spectra for the compounds investigated in this work. Only partial results have been obtained for 1, 3, 5-trinitrobenzene.

ANALYSIS

X-ray analysis of the crystal and molecular structure of nitrobenzene[11] reveals that the molecule is planar. Therefore it can be assumed that nitrogen enters into chemical bonding in an sp^2 hybridized state. Three of

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[b)]Based on the work performed by S. N. Subbarao in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University.

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TABLE I. Nitrogen-14 NQR spectra of several C-nitro compounds at 77 °K.

Compound	Formula	ν_+ (kHz)	ν_- (kHz)	e^2qQ (kHz)	η
1. Nitrobenzene	$C_6H_5NO_2$	1213	925	1425	0.404
2. *p*-dinitrobenzene	$C_6H_4(NO_2)_2$	1037	834	1247	0.326
3. *m*-dinitrobenzene		1030	812	1228	0.355
4. *p*-nitrobenzoic acid	$CO_2HC_6H_4NO_2$	982	812	1196	0.284
5. *m*-nitrobenzoic acid		1054	820	1249	0.375
6. *p*-nitroacetophenone	$COCH_3C_6H_4NO_2$	1127	885	1341	0.361
7. *m*-nitroacetophenone		1161	893	1369	0.391
8. Methyl-*p*-nitrobenzoate	$CO_2CH_3C_6H_4NO_2$	1120	853	1315	0.406
9. Methyl-*m*-nitrobenzoate		1150	886	1357	0.389
10. *p*-nitrobenzonitrile	$NCC_6H_4NO_2$	1116	875	1327	0.363
		3016[a]	2925[a]	3961[a]	0.046[a]
11. *m*-nitrocinnamic acid	$CHCHCO_2HC_6H_4NO_2$	1172	895	1378	0.402
12. *p*-nitroaniline	$H_2NC_6H_4NO_2$	1228	1012	1493	0.289
		2940[b]	2436[b]	3584[b]	0.281[b]
13. *m*-nitroaniline		1226	954	1453	0.374
		3215[b]	2593[b]	3872[b]	0.321[b]
14. *p*-nitrophenol	$HOC_6H_4NO_2$	1278	1006	1523	0.357
15. *m*-nitrophenol		1229	974	1469	0.347
16. *p*-nitrotoluene	$H_3CC_6H_4NO_2$	1198	911	1406	0.408
17. *m*-nitrotoluene		1190	910	1400	0.400
18. 2,6-dimethyl-4-nitrophenol	$(CH_3)_2OHC_6H_2NO_2$	1238	1000	1492	0.319
19. 2-chloro-4-nitrobenzoic acid	$ClC_6H_3NO_2CO_2H$	1044	837	1254	0.330
20. 2-chloro-5-nitrobenzoic acid		1062	844	1271	0.343
21. 2-chloro-4-nitrotoluene	$CH_3C_6H_3NO_2Cl$	1110	865	1317	0.372
22. 2,4,6-trinitrotoluene	$H_3CC_6H_2(NO_2)_3$	894	802	1131	0.163
		870	792	1108	0.141
		856	768	1083	0.163
23. Cholesteryl-*p*-nitrobenzoate	$COOC_{27}H_{45}C_6H_4NO_2$	1043	815	1239	0.368
24. *o*-nitrophenol		1127	918	1363	0.307
25. 1,3,5-trinitrobenzene[c]	$C_6H_3(NO_2)_3$	960	830		
		930			
26. Nitromethane	CH_3NO_2	1451	1091	1695	0.425

[a]Values for the cyano nitrogen.[10]
[b]Values for the amino nitrogen.
[c]Insufficient data.

the sp^2 orbitals form planar sigma bonds with the oxygens and the ring carbon. The remaining nitrogen p orbital forms a *pi* bond in which the aromatic electrons are largely delocalized.

The σ and π electron distributions in the vicinity of the nitrogen atom can be calculated in the framework of the theory proposed by Townes and Dailey.[12] However, it is necessary to know the directions and identities of the components of the efg tensor in its principal axis system. These directions and identities of q_{xx}, q_{yy}, and q_{zz} are not generally obvious, and measurements on single crystals may be required for the determinations.

Since many molecular orbital calculations[13–16] indicate a large delocalization of the π electrons at the nitrogen in nitrobenzene, it cannot be stated with certainty that the z axis is perpendicular to the plane of the molecule. Several NQR studies[10,17] have established that the electron density in an N–C sigma bond is in the range of

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TABLE II. sp^2 hybrid orbitals and occupation numbers for Case (1) of the principal axes shown in Fig. 1(a). $\gamma = \cot(\theta/2)$ and θ is the ONO bond angle.

Wavefunctions	Occupation numbers
$\psi_1 = \sqrt{[(1/2)(1-\gamma^2)]}s - \sqrt{(1/2)}p_x + \sqrt{(1/2)}\gamma p_z$,	σ_{NO}
$\psi_2 = \sqrt{[(1/2)(1-\gamma^2)]}s + \sqrt{(1/2)}p_x + \sqrt{(1/2)}\gamma p_z$,	σ_{NO}
$\psi_3 = \gamma s - \sqrt{(1-\gamma^2)}p_z$,	σ_{NC}
$\psi_4 = p_y$,	π

1.2–1.3 electrons. Therefore it is probable that the maximum contribution to the efg arises from the electrons in the N–C sigma bond. Thus the z direction of the principal axis system is chosen along the N–C bond direction. However, this assignment is open to question and should be considered as purely tentative. The x and y axes are then, of course, perpendicular to the N–C bond with one being in the plane of the molecule and one perpendicular to it. Arbitrarily (for the moment) labeling as x the axis in the plane, it is possible to write the bonding wave functions and the occupation numbers shown in Table II.

In the framework of the semiempirical Townes and Dailey theory[12] the quantities q_{xx}, q_{yy}, and q_{zz} are related to the occupation numbers of the nitrogen $2p$ orbitals by the equation[3]

$$q \equiv q_{zz} = \sum_i N_i [n_{zi} - (1/2)(n_{xi} + n_{yi})] q_p \ , \tag{4}$$

and similarly for q_{yy} and q_{xx}, where N_i is the number of nitrogen electrons in the bond described by ψ_i (occupation numbers in Table II), and n_x, n_y, and n_z are the weights of the p_x, p_y, and p_z orbitals, respectively, used in constructing ψ_i. The quantity q_p is the magnitude of the maximum component of the efg produced by a single $2p$ electron. Using Eq. (4) and the wavefunctions, one obtains

$$q = [(1-\gamma^2)\sigma_{NC} + (\gamma^2 - 1/2)\sigma_{NO} - (1/2)\pi] q_p \ , \tag{5}$$

$$q_{yy} = \{\pi - [(1+\gamma^2)/2]\sigma_{NO} - [(1-\gamma^2)/2]\sigma_{NC}\} q_p \ , \tag{6}$$

and

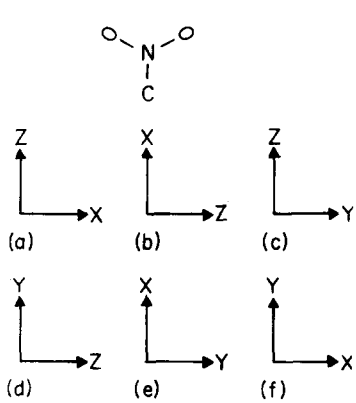

FIG. 1. Six possible cases for the principal axis system of the electric field gradient tensor at the nitrogen of the nitro group.

$$q_{xx} = \{[1 - (1/2)\gamma^2]\sigma_{NO} - [(1-\gamma^2)/2]\sigma_{NC} - (1/2)\pi\} q_p \ . \tag{7}$$

Equation (5) can be written as

$$(e^2qQ/e^2q_pQ) = [(1-\gamma^2)\sigma_{NC} + (\gamma^2 - 1/2)\sigma_{NO} - (1/2)\pi] \ . \tag{8}$$

From Eqs. (6) and (7), making use of Eq. (3), one obtains

$$(e^2qQ/e^2p_pQ)\eta = (3/2)(\sigma_{NO} - \pi) \ . \tag{9}$$

From Eq. (8) it can be seen that e^2qQ depends on the angle between the two N–O bonds. [Note: $\gamma = \cot(\theta/2)$.] Crystallographic data are not available for all of the compounds listed in Table I. But the available results[11,18–25] show that the bond angle ONO is greater than 120° by about 3°–4° in most of the compounds. Lucken,[2] and Schempp and Bray[3] have discussed the question of angular dependency and have come to the conclusion that, in an approximate theory such as the Townes and Dailey theory, consistent results are obtained if refinements concerning the exact bond angles are omitted. Guided by their results, θ is chosen to be 120°. Equation (8) now becomes

$$(e^2qQ/e^2q_pQ) = [(2/3)\sigma_{NC} - (1/6)\sigma_{NO} - (1/2)\pi] \ . \tag{10}$$

Solving Eqs. (9) and (10), and using Eqs. (1) and (2), the charge densities can be expressed in terms of the experimental frequencies as

$$\sigma_{NO} - \pi = (4/3)(\nu_d/e^2q_pQ) \ , \tag{11}$$

$$\sigma_{NC} - \sigma_{NO} = (2\nu_-)/e^2q_pQ \ . \tag{12}$$

Equations (11) and (12) have been obtained by choosing the z axis of the principal axes along the N–C bond direction and the y axis perpendicular to the plane of the ring. As was stated earlier, this choice of the principal axes is not unique. There are various other possibilities which have to be taken into consideration. But the choices are restricted by the following conditions: (a) one of the principal axes lies along the symmetry axis of the molecule[2] (i.e., the N–C bond direction), (b) σ_{NC} is greater than σ_{NO}. Condition (b) arises because oxygen is more electronegative than carbon. Imposition of condition (a) limits the possible choices for the principal axes to the six cases shown in Fig. 1. Case (1) has already been discussed at length. For the other cases one can proceed to write down the expressions for the electron densities in an exactly similar manner. The resulting expressions, after taking condition (b) into consideration, are collected in Table III where it can be seen that ν_d is a measure of $\sigma_{NC} - \sigma_{NO}$ in only two cases

TABLE III. Expressions for the electron densities at the nitrogen of the nitro group in terms of the experimental frequencies, for the six possible choices of the principal axis system shown in Fig. 1. Here $A \equiv e^2q_pQ$.

Cases	Figure	$\sigma_{NC} - \sigma_{NO}$	$\sigma_{NO} - \pi$	$\pi - \sigma_{NO}$
1.	1(a).	$2\nu_-/A$	$4\nu_d/3A$	
2.	1(b).	$2\nu_-/A$		$4\nu_+/3A$
3.	1(c).	$2\nu_+/A$		$4\nu_d/3A$
4.	1(d).	$2\nu_+/A$		$4\nu_-/3A$
5.	1(e).	$2\nu_d/A$		$4\nu_+/3A$
6.	1(f).	$2\nu_d/A$	$4\nu_-/3A$	

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[cases (5) and (6)]. Since ν_d is quite low (in the range of 300 kHz), this implies that $\sigma_{NC} - \sigma_{NO}$ is low in cases (5) and (6). In nitrobenzene ν_d is 288 kHz and calculations show that $\sigma_{NC} - \sigma_{NO} = 0.058$, assuming $e^2q_pQ = 10$ MHz. Since σ_{NC} is the range of 1.2–1.3[10,17] electrons, taking the lower limit of 1.20 for σ_{NC} leads to a value of about 1.14 for σ_{NO}. This value is high when it is expected that σ_{NO} should be less than 1 because oxygen is more electronegative than nitrogen. Even an unlikely value of 6 MHz for e^2q_pQ leads to a value of 1.1 electrons for σ_{NO}. In most of the other compounds ν_d is still smaller than 288 kHz, making σ_{NO} still higher. The value of σ_{NO} has been found to be 0.56 in isoazole[26] and 0.76–0.80 in oximes.[27] Therefore cases (5) and (6) can be ruled out as possible choices for the principal axis system. Consideration of the remaining four cases shows that $\sigma_{NC} > \sigma_{NO} > \pi$ in case (1), whereas in the other cases $\sigma_{NC} > \pi > \sigma_{NO}$.

Since NQR measurements give only two parameters (e^2qQ and η), it is not possible to calculate σ_{NO}, σ_{NC}, and π independently. However, several NQR studies[10,17] have estabished that σ_{NC} is in the range of 1.2–1.3 electrons. In the absence of a better alternative to remove the indeterminacy, it will be assumed that σ_{NC} is a constant and equal to 1.200 electrons. The quantity e^2q_pQ is not known accurately. Different authors have favored different values between 8 and 12 MHz.[2,3] In this work e^2q_pQ is assumed to be 8.4 MHz.[2,3,28] These are serious approximations when one is calculating the absolute electron densities, but are of negligible importance when comparisons are made of the electron distributions in similarly structed molecules.

Table IV lists the charge densities at the site of the nitrogen of the nitro group for all the four cases.

DISCUSSION

A. Nitromethane and nitrobenzene

The nitrogen-14 quadrupole coupling constant for the solid phase of nitromethane (1695 kHz; see Table I) is substantially larger than that obtained in the gaseous phase by microwave measurements (1180 kHz).[29,30] This result is rather surprising in view of the fact that the quadrupole coupling constant is expected to be smaller in the solid state than in the gaseous state because of lattice effects.[2] One explanation is the possibility of formation in the solid state of intermolecular hydrogen bonds of the type C–H ··· O, where C is the proton donor and O is the proton acceptor. In such a hydrogen bond, the electron density of the nonbonded orbital of the oxygen is decreased and the electron density of the C–H bond is increased by the contribution of the charge

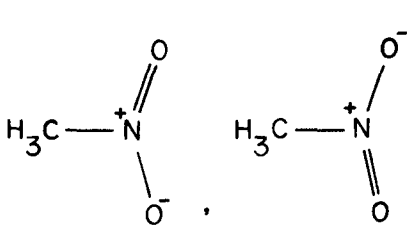

FIG. 2. Resonance structures of nitromethane.

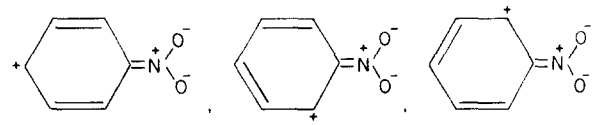

FIG. 3. Resonance structures of nitrobenzene.

transfer structure $C^- - H \cdots O^+$ with the result that the oxygens become more electronegative. Thus the oxygens are likely to attract the more mobile π electrons from the nitrogen resulting in reduced π electron density at the nitrogen. This implies that a loss of π density at the nitrogen leads to an increase in the coupling constant. It is reasonable to assume that in the absence of hydrogen bonding the coupling constant in the solid phase of nitromethane would be less than 1180 kHz. Comparing this with the coupling constant in nitrobenzene (1425 kHz) suggests that the π electron density at the nitrogen in nitrobenzene is less than that in nitromethane. This result is clearly not in accord with the fact that the nitro group, being an electron attracting group, withdraws electrons from the benzene ring. Therefore it is most unlikely that hydrogen bonds exist in the solid phase of nitromethane. In light of this discussion it is not clear why the quadrupole coupling constant in the solid phase of nitromethane should be larger than that in the gaseous phase. This suggests a re-examination of the microwave results.

Nitromethane can be written as a resonance hybrid of the structures shown in Fig. 2. There is no evidence of conjugation or hyperconjugation across the C–N bond.[30] Resonance theory predicts a positive charge on the nitrogen and negative charge on the oxygens. NQR results in all the four cases (Table IV) do indeed show that the total valence electron density ($\approx \pi + \sigma_{NC} + 2\sigma_{NO}$) at the nitrogen is less than 5 indicating that the nitrogen has acquired a net positive charge. The quantity σ_{NO} is appreciably higher than the values obtained in isoxazole[26] and oximes.[27] The explanation lies in the fact that the oxygen atoms, bearing net negative π charges, have reduced σ electronegativity resulting in increased σ_{NO}. The opposite is true in the case of oximes and isoxazole. In isoxazole, for example, the oxygen atom has one lone pair conjugating with the ring system and therefore bears a positive net π charge. The effect of this positive charge is to enhance the σ electronegativity of the oxygen atom thus reducing σ_{NO}.

Crystal structure studies of nitrobenzene by Trotter[11] show that the molecule is completely planar. But the C–N bond length is 1.486 Å which is somewhat longer than the usual value of 1.476 Å. This means that the C–N bond shows no shrinkage in nitrobenzene. This fact seems to be in conflict with the expectation that the C–N bond has double bond character due to the contribution from the polar resonance structures shown in Fig. 3. Thus Trotter threw doubt on the existence of a resonance interaction between the nitro group and the benzene ring.

However, a comparison of the electron distribution in nitromethane and nitrobenzene (compounds 26 and 1, respectively, of Table IV) shows that π and σ_{NO} at the nitrogen in nitrobenzene are larger than the corresponding

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TABLE IV. The electron densities at the nitrogen atom of the nitro group for all the four cases of the principal axis system discussed in the text. $e^2 q_p Q = 8.4$ MHz and $\sigma_{NC} = 1.200$ electrons. The numbers of the compounds are the same as in Table I.

Compound	$\sigma_{NC} - \sigma_{NO}$	$\sigma_{NO} - \pi$	σ_{NO}	π
Case (1)				
1	0.2202	0.0457	0.980	0.934
2	0.1986	0.0322	1.001	0.969
3	0.1933	0.0346	1.007	0.972
4	0.1933	0.0270	1.007	0.980
5	0.1952	0.0371	1.005	0.968
6	0.2107	0.0384	0.989	0.951
7	0.2126	0.0425	0.987	0.945
8	0.2031	0.0424	0.997	0.955
9	0.2110	0.0419	0.989	0.947
10	0.2083	0.0383	0.992	0.954
11	0.2131	0.0440	0.987	0.943
12	0.2410	0.0343	0.959	0.925
13	0.2271	0.0432	0.973	0.930
14	0.2395	0.0432	0.961	0.917
15	0.2319	0.0405	0.968	0.928
16	0.2169	0.0456	0.983	0.938
17	0.2167	0.0444	0.983	0.939
18	0.2381	0.0378	0.962	0.924
19	0.1993	0.0329	1.001	0.968
20	0.2010	0.0346	0.999	0.964
21	0.2060	0.0389	0.994	0.955
22	0.1910	0.0146	1.009	0.994
	0.1886	0.0124	1.011	0.999
	0.1829	0.0140	1.017	1.003
23	0.1940	0.0362	1.006	0.970
24	0.2186	0.0332	0.981	0.948
26	0.2598	0.0571	0.940	0.883
Case (2)				
1	0.2202	0.1925	0.980	1.172
2	0.1986	0.1646	1.001	1.166
3	0.1933	0.1635	1.007	1.171
4	0.1933	0.1559	1.007	1.163
5	0.1952	0.1673	1.005	1.172
6	0.2107	0.1789	0.989	1.168
7	0.2126	0.1843	0.987	1.172
8	0.2031	0.1778	0.997	1.175
9	0.2110	0.1825	0.989	1.172
10	0.2083	0.1771	0.992	1.169
11	0.2131	0.1860	0.987	1.173
12	0.2410	0.1949	0.959	1.154
13	0.2271	0.1946	0.973	1.168
14	0.2395	0.2029	0.961	1.163
15	0.2319	0.1951	0.968	1.163
16	0.2169	0.1902	0.983	1.173
17	0.2167	0.1889	0.983	1.172
18	0.2381	0.1965	0.962	1.158
19	0.1993	0.1657	1.001	1.166
20	0.2010	0.1686	0.999	1.168
21	0.2060	0.1762	0.994	1.170
22	0.1910	0.1419	1.009	1.151
	0.1886	0.1381	1.011	1.150
	0.1829	0.1359	1.017	1.153
23	0.1940	0.1656	1.006	1.172
24	0.2186	0.1789	0.981	1.160
26	0.2598	0.2303	0.940	1.170
Case (3)				
1	0.2888	0.0457	0.911	0.957
2	0.2469	0.0322	0.953	0.985
3	0.2452	0.0346	0.955	0.989

TABLE IV. (*Continued*)

Compound	$\sigma_{NC} - \sigma_{NO}$	$\pi - \sigma_{NO}$	σ_{NO}	π
Case (3)				
4	0.2338	0.0270	0.966	0.993
5	0.2510	0.0371	0.949	0.986
6	0.2683	0.0384	0.932	0.970
7	0.2764	0.0425	0.924	0.966
8	0.2667	0.0424	0.933	0.976
9	0.2738	0.0419	0.926	0.968
10	0.2657	0.0383	0.934	0.973
11	0.2790	0.0440	0.921	0.965
12	0.2924	0.0343	0.908	0.942
13	0.2919	0.0432	0.908	0.951
14	0.3043	0.0432	0.896	0.939
15	0.2926	0.0405	0.907	0.948
16	0.2852	0.0456	0.915	0.960
17	0.2833	0.0444	0.917	0.961
18	0.2948	0.0378	0.905	0.943
19	0.2486	0.0329	0.951	0.984
20	0.2529	0.0346	0.947	0.982
21	0.2643	0.0389	0.936	0.975
22	0.2129	0.0146	0.987	1.002
	0.2071	0.0124	0.993	1.005
	0.2038	0.0140	0.996	1.010
23	0.2483	0.0362	0.952	0.988
24	0.2683	0.0332	0.932	0.965
26	0.3455	0.0571	0.855	0.912
Case (4)				
1	0.2888	0.1468	0.911	1.058
2	0.2469	0.1324	0.953	1.086
3	0.2452	0.1289	0.955	1.084
4	0.2338	0.1289	0.966	1.095
5	0.2510	0.1302	0.949	1.079
6	0.2683	0.1405	0.932	1.072
7	0.2764	0.1417	0.924	1.065
8	0.2667	0.1354	0.933	1.069
9	0.2738	0.1406	0.926	1.067
10	0.2657	0.1389	0.934	1.073
11	0.2790	0.1421	0.921	1.063
12	0.2924	0.1606	0.908	1.068
13	0.2919	0.1514	0.908	1.060
14	0.3043	0.1597	0.896	1.055
15	0.2926	0.1546	0.907	1.062
16	0.2852	0.1446	0.915	1.059
17	0.2833	0.1444	0.917	1.061
18	0.2948	0.1587	0.905	1.064
19	0.2486	0.1329	0.951	1.084
20	0.2529	0.1340	0.947	1.081
21	0.2643	0.1373	0.936	1.073
22	0.2129	0.1273	0.987	1.114
	0.2071	0.1257	0.993	1.119
	0.2038	0.1219	0.996	1.118
23	0.2483	0.1294	0.952	1.081
24	0.2683	0.1457	0.932	1.077
26	0.3455	0.1732	0.855	1.028

values for nitromethane. This implies that the nitro group has indeed withdrawn electrons from the benzene ring, both by induction and resonance.

B. Substituted nitrobenzenes

Substituents are commonly grouped as electron attracting or electron donating relative to hydrogen. When a substituent replaces hydrogen on the nitrobenzene mol-

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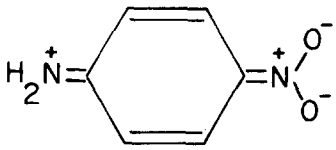

FIG. 4. Resonance structure of p-nitroaniline.

ecule in the para position, it is capable of entering into resonance conjugation with the nitro group resulting in enhanced or reduced π electron density at the nitrogen of the nitro group depending upon whether the substituent is electron donating or electron withdrawing. On the other hand, substituents in the meta position are structurally unable to enter into resonance conjugation with the nitro group. Therefore it is expected that the π electron density at the nitrogen of the nitro group is very little affected by a substituent in the 3-position.

Examination of Table IV shows that these expectations are largely realized in case (2), with a few exceptions which will be explained later. On the other hand, cases (1), (3), and (4) show substantial increases in the π electron density at the nitrogen of the nitro group when there is an electron withdrawing substituent on the nitrobenzene molecule. In addition, in cases (1), (3), and (4) there is a large variation in the π density at the nitrogen of the nitro group when there is a substituent in the meta position, whereas case (2) shows a notable uniformity.

These considerations suggest that the most probable choice for the principal axis system is the one corresponding to case (2). However, it should be noted that the microwave studies of nitromethane[29,30] give the principal axis system for the efg tensor at the nitrogen as the one corresponding to case (1) discussed here. But, as pointed out earlier, there is a substantial disagreement in the quadrupole coupling constant of nitromethane as measured by microwave and pulsed NQR techniques. In the following discussion the principal axis system has been taken to be the one corresponding to case (2) [Fig. 1(b)].

In p-nitroaniline, the amino group is almost coplanar with the ring and enters into conjugation with the ring system and the nitro group.[19] NQR data reflect this trend. The quadrupole coupling constant for the amino nitrogen in p-nitroaniline (3584 kHz) is lower than that found in aniline (3932 kHz)[31] in which the amino nitrogen is sp^3-like.[32] A lower value for e^2qQ means a more nearly spherical charge distribution because of the electron loss from the lone pair. In valence bond terms this can be attributed to the importance of the resonance forms of the type shown in Fig. 4. Such a resonance interaction between the nitro group and the electron donating amino group should lead to an enhancement of π electron density at the nitrogen of the nitro group compared with nitrobenzene. However, NQR results show [Table IV, case (2)] that π electron density at the nitro group nitrogen is lower than that in nitrobenzene. Also, the same trend is observed in the case of p-nitrophenol where because of the resonance interaction between the electron releasing hydroxyl group and the nitro group it was expected that there would be higher π electron density at the nitrogen compared with nitrobenzene.

Crystal structure studies of p-nitroaniline[18,19] and p-nitrophenol[22,23] reveal intermolecular hydrogen bonds of the type N–H ··· O between the amino group and the nitro group in p-nitroaniline and of the type O–H ··· O between the hydroxyl group and oxygens of the nitro group in p-nitrophenol. Such hydrogen bonds make the oxygens of the nitro group more electronegative. This results in the oxygens attracting the more mobile π electrons from the nitrogen of the nitro group. Thus the reduced π density at the nitro group nitrogen compared to that in nitrobenzene is probably due to intermolecular hydrogen bonds in p- nitroaniline and p- nitrophenol.

In m-nitroaniline the quadrupole coupling constant for the amino nitrogen (3872 kHz) is not much lower than that in aniline. This suggests that there is very little conjugation between the amino group and the ring. Therefore, it is expected that there would be very little change in the π electron density at the nitrogen of the nitro group. However, NQR results show [Table IV, case (2)] a slight decrease in the π electron density compared to nitrobenzene. This decrease is probably due to weak intermolecular hydrogen bonds between the amino group and the nitro group, as indicated by an x-ray study of m- nitroaniline.[33] The decrease in the π electron density is much smaller in m-nitroaniline than in p-nitroaniline. This suggests that the hydrogen bonds are much weaker in m-nitroaniline than in p-nitroaniline.

NQR results for the cyano nitrogen in p-nitrobenzonitrile reported by Colligiani *et al.*,[10] indicate that the cyano nitrogen has lost π electrons compared to benzonitrile. Examination of Table IV, case (2) reveals that the nitrogen of the nitro group has also lost π electrons compared to nitrobenzene. This suggests that the two electron attracting groups para to each other are competing for the ring electrons. This is similar to the situation in 4-cyanopyridine where the two electron attracting groups act against each other to give reduced π density on each.[28]

The methyl group is known to be electron donating by hyperconjugation. However, NQR results [Table IV, case (2)] in the nitrotoluenes indicate that the hyperconjugation effect of the methyl group is negligible. This is in accord with the results of nitrogen chemical shift measurements in nitrotoluenes[34] and also with the crystal structure determination of p-nitrotoluene.[20]

The discussion so far has been confined to determining the effect of the various substituents on the π electron distribution at the nitrogen of the nitro group. However, the variation of σ_{NO} in the various compounds is not in accord with the known induction effect of the substituents. For example, the nitro group is known to be sigma electron attracting by induction. Therefore, σ_{NO} is expected to be less in the dinitrobenzenes than in nitrobenzene. But Table IV shows that σ_{NO} in the dinitrobenzenes is larger than that found in nitrobenzene.

From Table III, case (2),

$$\sigma_{NC} - \sigma_{NO} = 2\nu_-/e^2q_pQ \ , \tag{13}$$

and

$$\pi - \sigma_{NO} = 4\nu_+/3e^2q_pQ \ . \tag{14}$$

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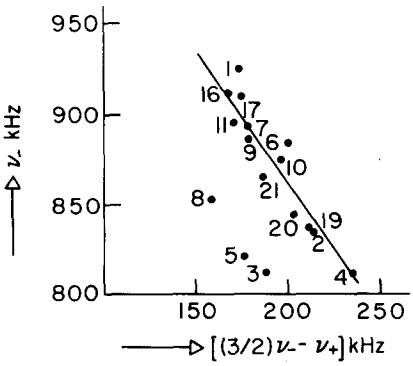

FIG. 5. Plot of $[(3/2)\nu_- - \nu_+]$ against ν_-. The numbers on the plot are the same as the numbers of the compounds in Table I.

From Eqs. (13) and (14) one obtains

$$\sigma_{NC} - \pi = 4[(3/2)\nu_- - \nu_+]/(3e^2 q_p Q) \ . \qquad (15)$$

A plot of ν_- which is a measure of $\sigma_{NC} - \sigma_{NO}$ [see Eq. (13)] against $[(3/2)\nu_- - \nu_+]$ which is a measure of $\sigma_{NC} - \pi$ is shown in Fig. 5. The equation for the straight line shown on the plot, obtained by the method of least squares (excluding the points 3, 5, and 8), is

$$\nu_- = -1.55[(3/2)\nu_- - \nu_+] + 1172 \quad (n = 13) \ ,$$

with a correlation coefficient $r = 0.93$ and the standard deviation from the line $s = 13.6$ kHz; n is the number of points used in the regression analysis. It is not clear why points 3, 5, and 8 show considerable scattering from the other points. But it is seen that even these points show a trend similar to the trend shown by the rest of the points. To better understand the correlation shown in Fig. 5, σ_{NC} will be assumed to be a constant. This is the same approximation made earlier to calculate σ_{NO} and π electron densities. The trend appears to be that as the π electron density at the nitrogen decreases the σ_{NO} density increases. The explanation is probably due to the enhanced electronegativity of nitrogen as the π electron density decreases. It is apparent, therefore, that the distribution of σ electron density is mainly controlled by the interaction between π and σ electrons. Similar conclusions have been arrived at by Howe[15] in his all-valence-electron calculations for mono substituted benzenes. It should be noted that most of the theoretical calculations ignore the σ electrons completely. Absence of correlations of the σ electron density with the inductive effect of the substituents in the pyridines has been reported by Schempp and Bray.[28] These authors point out that chemical evidence concerning the so-called inductive effects is rather indirect.

C. Correlations of NQR data with Hammett σ parameters[6,35-38]

As the Hammett σ constant[6] is a measure of the ability of a substituent to withdraw electrons from, or supply electrons to, a reaction site, several attempts have been made to correlate σ with NQR frequencies.[28,39-43] In a study of chlorine-35 NQR in singly substituted chlorobenzenes, Meal[39] noted an apparent linear correlation between the frequencies and the Hammett σ values of the substituents. Extension of this work to a large number of chlorobenzenes and bromobenzenes by Bray and co-worker[40-43] has verified the linear relationship between the frequencies and the σ constants. Since the Hammett σ constant is a measure of the total electronic effect of a substituent, attempts have been made to separate the Hammett σ constant into inductive (σ_I) and resonance (σ_R) parts.[37] In the present work, correlations of NQR data with these parameters are considered.

From Eq. (15) it can be seen that $[(3/2)\nu_- - \nu_+]$ is a measure of $\sigma_{NC} - \pi$. Since σ_{NC} is assumed to be a constant it is felt that $[(3/2)\nu_- - \nu_+]$ should correlate with σ_R the resonance contribution to the Hammett σ constant. Table V lists the frequencies $[(3/2)\nu_- - \nu_+]$ for the substituted nitrobenzenes with the available corresponding σ and σ_R values, with nitrobenzene as the standard. Electron attracting groups such as the nitro group have positive σ(or σ_R) values, whereas electron releasing groups such as the amino group have negative σ (or σ_R) values.[6,37] Figure 6 shows a plot of $[(3/2)\nu_- - \nu_+]$ against σ_R. The numbers on the figure correspond to the numbers of the compounds in Table V, The least squares equation of the line on the plot is given by

$$[(3/2)\nu_- - \nu_+] = 178 + 160\sigma_R \quad (n = 10) \ ,$$

with a correlation coefficient $r = 0.92$ and the standard deviation from the line $s = 6.6$ kHz. The expected trend, in which π decreases as σ_R increases, is clearly evident. Points 12–14 (not shown on the plot) show considerable scattering from the other points. This is as expected because of hydrogen bonds in these compounds, as discussed earlier. Points 15 and 18 also show similar scattering, suggesting the possibility of hydrogen bonds in these compounds. An x-ray study of m-nitrophenol[24] (point 15) indicates weak hydrogen bonds in this compound.

As pointed out earlier, the variation of σ_{NO} is not in accord with the inductive effect of the substituents. Moreover, σ_{NO} shows a decided trend to vary with the π electron density. It is apparent, therefore, that there would be no correlation between σ_I (the inductive contribution to the Hammett σ constant) and NQR data. It should be noted that in arriving at the σ_R values the assumption has been made[37] that σ_I is the same for a substituent in the meta and para positions. Since ν_- is a measure of $(\sigma_{NC} - \sigma_{NO})$, inspection of Table I does indicate that in many cases the ν_- values for the meta and para isomers of the same compound are close to each other.

Since σ_R is obtained by subtracting σ_I from σ, it is

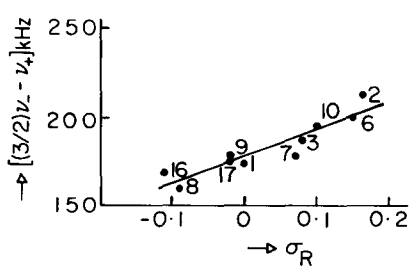

FIG. 6. Plot of $[(3/2)\nu_- - \nu_+]$ against σ_R, the resonance contribution to the Hammett σ constant. The numbers on the plot are the same as the numbers of the compounds in Table V.

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TABLE V. NQR frequencies $[(3/2)\nu_- - \nu_+]$ and the available corresponding Hammett σ and σ_R values.

Compound	Substituent	$[(3/2)\nu_- - \nu_+]$ (kHz)	σ[a]	σ_R[b]
1. Nitrobenzene	H	170.5	0	0
2. p-dinitrobenzene	p-NO_2	214	1.27[c]	0.16
3. m-dinitrobenzene	m-NO_2	188	0.71	0.08
4. p-nitrobenzoic acid	p-COOH	236	0.73[c]	···
5. m-nitrobenzoic acid	m-COOH	176	0.37	···
6. p-nitroacetophenone	p-$COCH_3$	200.5	0.87[c]	0.15
7. m-nitroacetophenone	m-$COCH_3$	178.5	0.38	0.07
8. Methyl-p-nitrobenzoate	p-$COOCH_3$	159.5	0.31	−0.09
9. Methyl-m-nitrobenzoate	m-$COOCH_3$	179	0.39	−0.02
10. p-nitrobenzonitrile	p-CN	196.5	0.66	0.10
11. m-nitrocinnamic acid	m-CHCHCOOH	170.5	0.14[d]	···
12. p-nitroaniline	p-NH_2	290	−0.66	−0.76
13. m-nitroaniline	m-NH_2	205	−0.16	−0.25
14. p-nitrophenol	p-OH	231	−0.37	−0.60
15. m-nitrophenol	m-OH	232	0.12	−0.17
16. p-nitrotoluene	p-CH_3	168.5	−0.17	−0.11
17. m-nitrotoluene	m-CH_3	175	−0.07	−0.02
18. 2,6-dimethyl-4-nitrophenol	p-OH + 2m-CH_3	262	−0.51	−0.64
19. 2-chloro-4-nitrobenzoic acid	p-COOH + m-Cl	211.5	1.10	···
20. 2-chloro-5-nitrobenzoic acid	p-Cl + m-COOH	204	0.60	···
21. 2-chloro-4-nitrotoluene	p-CH_3 + m-Cl	187.5	0.24	···

[a]Hammett σ values are taken from Ref. 36 unless noted otherwise.
[b]σ_R values are taken from Ref. 37.
[c]These values are taken from Ref. 35.
[d]This value is taken from Ref. 38.

strange that σ_R should correlate with the NQR data but not σ_I. A plot of $[(3/2)\nu_- - \nu_+]$ against the Hammett σ constant is shown in Fig. 7. The least squares equation for the straight line shown on the plot is

$$[(3/2)\nu_- - \nu_+] = 170 + 34\sigma \quad (n = 15) \ ,$$

with a correlation coefficient $r = 0.86$ and the standard deviation from the line $s = 8.7$ kHz. The numbers on the plot correspond to the compounds listed in Table V. Linear additivity of sigma values has been assumed in cases of multiple substitutions. Points 4, 12–15, and 18 (not shown on the plot) show considerable scattering from the other points. There is some doubt as to the correctness of the σ_p value for the COOH group (point 4).[36] Since there are hydrogen bonds in compounds corresponding to points 12–15 the scattering is expected as discussed earlier. Point 18 also shows similar scattering suggesting the possibility of hydrogen bonds in this compound, a conclusion reached earlier in connection with the correlation of $[(3/2)\nu_- - \nu_+]$ with σ_R.

For the purpose of predicting unknown σ and σ_R values the following equations can be used:

$$\sigma_R = 0.0053[(3/2)\nu_- - \nu_+] - 0.94 \ ,$$

with $s = 0.035$ and $\sigma = 0.022[(3/2)\nu_- - \nu_+] - 3.59$, with $s = 0.21$. Using these two equations, σ_R and σ for the cholesteryl group can be estimated. It turns out that $\sigma_R = 0.011$ and $\sigma_p = 0.36$. This suggests that the cholesteryl group is an electron attracting group.

CONCLUSIONS

It is appropriate to conclude that NQR techniques can be successfully employed to determine the influence of substituents on charge densities. In the C-nitro compounds studied in this work, the choice of the principal axis system for the efg tensor at the nitrogen is not obvious. Therefore, all the six possible cases have been considered. The results lead to the conclusions that the most probable choice for the principal axes in the one shown in Fig. 1(b) corresponding to case (2) discussed in the text. However, it should be pointed out that this conclusion about the principal axis system is completely different from that obtained from a study of nitromethane by microwave measurements[29,30] which give the assignment of the principal axes as the one corresponding to case (1) shown in Fig. 1(a). In addition, the coupling constant in the solid phase of nitromethane (1695 kHz) is substantially larger than that found in the gaseous phase by microwave measurements (1180 kHz). This difference cannot be explained by taking into consideration the existence of possible hydrogen bonds in the solid phase of nitromethane. A single crystal NQR measurement and a re-examination of the microwave data are clearly in order.

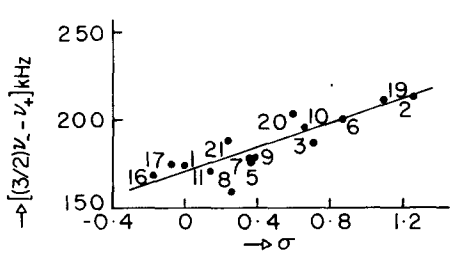

FIG. 7. Plot of $[(3/2)\nu_- - \nu_+]$ against the Hammett σ constant. Numbers on the plot are the same as the numbers of the compounds in Table V.

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The variation of the π electron density at the nitrogen with the substituents is in very good agreement with the ideas of classical chemistry with a few exceptions in which there are intermolecular hydrogen bonds. Satisfactory correlations of NQR data with σ and σ_R suggest that the Hammett σ constant is largely a measure of the ability of a substituent to withdraw or donate π electrons to a reaction site. It is apparent that the Hammett σ constant cannot be used in cases where there are hydrogen bonds. NQR data reveal that the cholesteryl group is an electron attracting group with $\sigma_p = 0.36$ and $\sigma_R = 0.011$.

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