AM1 Calculations of Rotation around Essential Single Bonds and Preferred Conformations in Conjugated Molecules

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Equilibrium twist angles, rotational barriers around essential single bonds, and preferred conformations for over 60 conjugated organic molecules were calculated using the semiempirical AM1 (Austin model 1) method. Comparison with *ab initio* and experimental data shows that AM1 can be applied quite successfully to conformational problems of this type. Relatively large errors are, however, found for compounds in which lone pair–hydrogen and especially lone pair–lone pair interactions are decisive for their conformational behavior. AM1-calculated rotational barriers in conjugated molecules, however, are found to be much too low. Moreover, AM1 does not seem to even correctly reproduce the trend of rotational barriers within a series of structurally related compounds. *E/Z* energy differences obtained by AM1 are also frequently considerably too low. In contrast to rotational barriers, their trends and thus conformational preferences, however, are quite satisfactorily calculated by this method. Ionization potentials obtained by AM1 are too high by about 0.5 eV. However, trends are quite well predicted.

I. INTRODUCTION

Despite the successful application of the semiempirical MNDO method[1] in many areas of computational chemistry (for some recent critical compilations concerning the performance of MNDO, cf. ref. 2) a number of weaknesses, such as failure to reproduce hydrogen bonds, activation energies that tend to be too large, energies that are too negative for four-membered rings, have been reported.[1] Recently, Dewar *et al.*[3] have proposed a new version of MNDO [Austin model 1 (AM1)] in which the errors associated with MNDO seem to have been largely corrected. According to Dewar's group,[3] the common cause of the errors with MNDO is due mostly to an overestimation of nonbonded repulsions. A direct consequence is the fact that MNDO does not give even qualitatively correct potential functions for rotations about essential single bonds in conjugated molecules, typically favoring perpendicular or nearly perpendicular arrangements of the two molecular parts.[1,3,4] Similar problems arise with almost all other semiempirical methods.[5]

In attempts to rationalize the ultraviolet absorption spectra of organic dyes (e.g., benzopyrroles and -dipyrroles[6a] or pyrazolone derivatives[6b]), we frequently encounter conformational problems in conjugated molecules. Similarly, in a project currently under investigation concerning the thermal stability of polymers containing the enaminocarbonyl unit, we plan to study rotational barriers in compounds of this type. The size of the molecules of interest to us clearly prevents the use of *ab initio* methods. Thus we are strongly interested in inexpensive yet reliable as well as effective procedures for the study of conformational problems. The rather limited examples of AM1 calculations of rotational barriers around essential single bonds in conjugated molecules[3,4b,d] indicate that this method might be useful for our purpose. In view of the very general importance of conformational equilibria in ultraviolet spectroscopy,[4g,6c,d] photophysical processes,[4e,5c,d] chemical reactivity,[4a,14] nuclear magnetic resonance (NMR) spectroscopy,[4f,6e,f] biological activity,[6d] as well as many other areas of chemistry,[6g–k] we found it worthwhile to investigate in somewhat greater detail the performance of AM1 in this connection. Here we report AM1 calculations on a set of more than 60 compounds selected to represent the most commonly found types of rotational isomerism in conjugated molecules and for which experimental and/or *ab initio* data were available.

II. COMPUTATIONAL DETAILS

All calculations were carried out using the AMPAC program package.[7] Except where otherwise noted (Table I), conformational energies were computed in steps of 30° for the dihedral angle θ and fitted[8] to a six-term Fourier expansion (1):

$$\delta E = E(\theta) - E(0°) = 1/2 \sum V_j(1 - \cos j\theta)$$

(1)

With the exception of aromatic rings which were assumed to be planar, all remaining geometric parameters were completely optimized. To test the adequacy of this approach, in any case, additional points on the reaction coordinate θ were calculated. No significant deviations of these additional points from the potential function (1) could be found.

III. RESULTS

The AM1 calculation results (dihedral angles θ and energies [kJ/mol]) for minima and barriers are compiled in Table I. Also listed are the corresponding *ab initio* and/or experimental quantities. Compounds **60–64** for which neither experimental nor *ab initio* data seem to be available were included because of their interesting chemical properties.[4a] According to eq. (1) in Table I, all energies are given relative to the planar conformation with $\theta = 0°$ (except for *cis*-stilbene where $\theta = 0°$ is sterically impossible). For all compounds exhibiting E/Z-isomerism [i.e., $E(0°) \neq E(180°)$] the dihedral angle $\theta = 0°$ corresponds to the Z conformation. Since the conformational behavior of conjugated molecules is strongly affected by the medium, for example, the well known case of biphenyl which is found to be planar in the solid state[16a] and twisted both in solution[16b] and in the gas phase[10g] whenever available comparison in Table I is made to experimental results obtained in the gas phase. Furthermore, the experimentally determined barriers to rotation[10g,h,16b] as well as the preferred conformations (E vs. Z)[11f-i] depend on the physical state of the system. In addition, equilibrium twist angles θ_{min} obtained by fitting the experimental data to a truncated Fourier series (1) may be sensitive to the number of terms retained in (1).[15a] Minimal basis set *ab initio* calculations are

claimed to give at least qualitatively correct potential energy functions for internal rotation in conjugated molecules,[15a] although STO-3G seems to overestimate conjugative interactions thus leading to rotational barriers which are somewhat too high, especially in the rigid rotor approximation.[9d,q,15] However, it is not completely clear whether larger basis sets will give improved results: in a number of cases, STO-3G computations yield much closer agreement with experimental results than do calculations using the 4-31G, 6-31G, or even 6-31G* basis.[9p,r] Thus, in the following discussion one should keep in mind that eventual discrepancies between AM1 results and either *ab initio* calculations or experimental findings need not necessarily be due to shortcomings of AM1 alone.

IV. DISCUSSION

Because experimental data are frequently available only for equilibrium twist angles (cf. Table I) we will first focus our attention to the performance of AM1 with respect to calculations of θ_{min}. Following this discussion we will consider rotational barriers and finally E/Z energy differences. In addition, according to a suggestion of one referee, the performance of AM1 with respect to ionization potentials will also be discussed.

Torsional Angles

As can be seen from the data of Table I, AM1 generally leads to equilibrium twist angles which compare quite satisfactorily with both *ab initio* as well as experimental data. Closer inspection of Table I reveals some discrepancies which need further discussion. In contrast to earlier work on butadiene[10a] which assigned the planar s-trans and s-cis conformations, respectively, for the two stable rotamers of **1**, previous semiempirical calculations[5c] led to a gauche minimum for the second rotamer ($\theta \approx 35°$). Using AM1 this gauche minimum nearly completely vanishes in favor of a planar conformation. *Ab initio* results depend on the basis set used: STO-3G calculations[9a] yield $\theta_{min} \approx 0°$ like AM1, whereas larger basis sets[9a-c] predict a gauche rather than a planar conformation for (Z) butadiene ($\theta = 38°$). Recent experimental evidence, however, is in favor of a C_{2v} geometry for (Z)-**1** ($\theta_{min} <$

Table I. Twist angles (degrees) and (in parentheses) energies (kJ/mol) for minima and barriers.

Compound	AM1		Ab initio[a]		Experimental[b]	
	Minima	Barriers	Minima	Barriers	Minima	Barriers
Butadiene (1)[c]	10 (−0.02)	0	38 (−4.03)	0	0	(19.51)
	180 (−3.24)	88 (5.09)	180 (−16.26)	102 (9.18)	180 (−10.44)	
Styrene (2)	18 (−0.39)	0	0	90 (13.1)	0	90 (13.7)
		90 (5.81)				
2-Vinylpyridine (3)	0	97 (8.23)	0	90 (22.80)	0	
	150 (4.30)	180 (5.13)	180 (5.02)			
3-Vinylpyridine (4)	0	90 (6.47)	0	90 (15.81)		
	180 (−0.23)		180 (−1.17)			
4-Vinylpyridine (5)	18 (−0.11)	0	0	90 (17.32)	0	
		90 (5.51)				
6-Methyl-6-phenyl-fulven (6)	51 (−30.22)	0	~80 (MNDO[4f])		58	
		90 (−27.45)				
Cis-stilbene (7)[d]	52 (0.0)	90 (2.95)	52		43	
Trans-stilbene (8)	22 (−0.64)	0	19		33	
		90 (12.88)				
Biphenyl (9)	41.4 (−8.97)	0	43 (−13.0)	0	44.4 (−6.0)	0
		90 (−4.36)		90 (−4.09)		90 (0.5)
2-Phenylpyridine (10)	40 (−5.82)	0	33 (−4.61)	0	30	
		90 (−1.01)		90 (8.70)		
4-Phenylpyridine (11)	40 (−7.54)	0	43 (−17.2)	0	~0[(10i)]	
		90 (−3.11)		90 (−8.1)	40[(10l)]	
2-Phenylpyrimidine (12)	36 (−2.18)	0	0	90 (22.5)	<15	
		90 (3.10)				
4-Phenylpyrimidine (13)	38 (−4.64)	0	33 (−5.02)	0		
		90 (0.54)		90 (9.20)		
5-Phenylpyrimidine (14)	38 (−5.93)	0	43 (−17.96)	0		
		90 (−0.93)		90 (−8.20)		
2,2'-Bipyridine (15)	55 (−11.81)	0	45 (−16.5)	0	180[(10k)]	
	142 (−17.46)	74 (−11.41)	180 (−39.7)	84 (−10.3)	160[(10l)]	
		180 (−15.09)				
2,3'-Bipyridine (16)	37 (−4.21)	0	35 (−6.4)	0	32	
	142 (−5.03)	88 (0.92)	145 (−7.4)	90 (6.6)	122	
		180 (−0.38)		180 (−1.1)		
2,4'-Bipyridine (17)	39 (−4.86)	0	33 (−5.0)	0		
		90 (−0.41)		90 (8.6)		
3,3'-Bipyridine (18)	38 (−6.05)	0	41 (−13.3)	0	>0[h]	
	142 (−6.39)	89 (−1.21)	139 (−13.8)	89 (−3.2)		
		180 (−0.45)		180 (−0.8)		
3,4'-Bipyridine (19)	38 (−6.11)	0	40 (−11.2)	0		
		90 (−1.34)		90 (−0.6)		
4,4'-Bipyridine (20)	40 (−6.57)	0	41 (−11.0)	0	45[(10k)]	
		90 (−2.49)		90 (−2.1)	37[(12)]	
					36 (−10.7)[(10z)]	0[(10z)]
						90 (9.2)[(10z)]
2,2'-Pyridyl-pyrimidine (21)	60 (−7.97)	0	≤15 (NDDO[13])			
		90 (−7.47)				
2,2'-Bipyrimidine (22)	90 (−18.42)	0	40 (−3.44)	0	41[(10n)]	
				90 (2.16)	48[(10o)]	
4,4'-Bipyrimidine (23)	55 (−9.86)	0	50 (−19.1)	0		
	147 (−16.09)	70 (−9.73)	180 (−38.8)	92 (−9.7)		
		180 (−14.48)				
4,5'-Bipyrimidine (24)	32 (−2.10)	0	28 (−2.2)	0		
		90 (4.94)		90 (12.5)		
5,5'-Bipyrimidine (25)	35 (−3.83)	0	42 (−12.5)	0		
		90 (1.25)		90 (−3.8)		
2-Phenylfuran (26)	0	90 (10.25)			0	
3-Phenylfuran (27)	19 (−0.19)	0			~30	
		90 (5.41)				
1-Phenylpyrrole (28)[e]	28 (−1.6)	0			~0	
		90 (6.79)				
2-Phenylpyrrole (29)[e]	27 (−0.8)	0				
		90 (5.27)				
3-Phenylpyrrole (30)[e]	19 (−0.2)	0				
		90 (6.58)				

Table I. (*continued*)

Compound	AM1		Ab initio[a]		Experimental[b]	
	Minima	Barriers	Minima	Barriers	Minima	Barriers
1-Phenylpyrazole (31)	27 (−1.09)	0 90 (7.12)			0–28[(10q,r)]	
1-Phenylimidazole (32)	27 (−1.23)	0 90 (5.56)			~0	
1-Phenylmaleinimide (33)[f]	28 (−2.36)	0 90 (6.60)			44	
1-Phenyltriazolindione (34)[f]	23 (−0.75)	0 90 (6.94)	45	0 90		
2,2′-Bifuran (35)	0 180 (0.83)	92 (10.57)	0 180 (−3.39)	90 (15.34)	0 180	
2,3′-Bifuran (36)	0 180 (0.89)	93 (9.66)	0 180 (0.66)	89 (17.76)		
3,3′-Bifuran (37)	0 180 (−0.01)	91 (5.75)	0 180 (−0.56)	91 (13.58)		
1,1′-Bipyrrole (38)	90 (−11.76)	0	90 (−21.3)	0	90	
2,2′-Bipyrrole (39)	27 (−0.23) 180 (−5.13)	0 81 (1.41)	26 (−0.79) 180 (−12.05)	0 84 (7.25)	180	
2,3′-Bipyrrole (40)	0 180 (−2.27)	85 (5.54)	0 180 (−2.46)	86 (14.21)		
3,3′-Bipyrrole (41)	0 180 (−0.57)	88 (6.81)	0 180 (−1.01)	90 (14.61)		
Acrolein (42)	0 180 (−0.90)	88 (6.55)	0 180 (−2.0)	(20.4)	0 180 (−6.98)	(19.76)
Methacrolein (43)	0 180 (2.26)	92 (8.13)	0 180 (−1.16)	(21.4)	0 180 (−9.09)	(36.91)
Glyoxal (44)	180 (−10.33)	0	0 180 (−6.3)	88 (12.0)	0 180 (−14.14)	
Benzaldehyde (45)	0	90 (11.17)	0	90 (24.5)	0	90 (19.3)
Benzophenone (46)[d]	32 (−37.27)	0 90 (−25.36)	32 (−33.7)	0 90 (−9.1)	30	
Furan-2-carboxaldehyde (47)	0 180 (−3.77)	89 (13.93)	0 180 (−3.5)	90 (26.3)	0 180 (−8.5)	(25.0)
Furan-3-carboxaldehyde (48)	0 180 (3.04)	93 (14.90)	0 180 (0.6)	91 (24.5)	180	
Pyrrole-2-carboxaldehyde (49)	0 180 (13.40)	98 (29.45)	0 180 (7.8)	91 (39.2)	0	
Pyrrole-3-carboxaldehyde (50)	0 180 (3.95)	93 (18.43)	0 180 (1.55)	91 (28.0)	180	
Pyridine-2-carboxaldehyde (51)	42 (−0.36) 180 (−8.04)	78 (0.03)	0 180 (−10.23)	86 (18.7)	180	
Pyridine-3-carboxaldehyde (52)	0 180 (−0.79)	89 (11.54)	0 180 (−1.53)	90 (25.1)	180	
Pyridine-4-carboxaldehyde (53)	0	90 (8.42)	0	90 (25.3)	0	90 (16.02)
Benzoic acid (54)	0	90 (11.80)	0	90 (24.22)	2	
Benzamide (55)	36 (−1.70)	0 90 (2.34)	30 (−3.31)	0 90 (8.79)	28[(6e)] 39[(11m)]	
Nitroethene (56)	0	90 (11.81)	0	90 (20.1)	0	90 (20.22)
Nitrobenzene (57)	0	90 (14.53)	0	90 (20.9)	0	90 (13.6)
1,4-Dinitrobenzene (58)	0	90 (26.93)			7	
1,5-Dinitronaphthalene (59)	32 (−4.23)	0 90 (11.70)			49	
1-Phenylpyridinium cation (60)	49 (−17.11)	0 90 (−15.19)	90 (MNDO[4a])			
4-OH-1-Phenylpyridinium cation (61)	50 (−17.59)	0 90 (−16.16)	89 (MNDO[4a])			
2-OH-1-Phenylpyridinium cation (62)	50 (−27.18)	0 90 (−26.64)	89.8 (MNDO[4a])			
1-Phenylpyrazolium cation (63)	90 (−7.90)	0	85 (MNDO[4a])			
1-Phenylimidazolium cation (64)	42 (−4.37)	0 90 (−3.00)	85 (MNDO[4a])			
4,4′-Bipyridinium dication (65)	45 (−8.21)	0 90 (−6.71)	45 (−16.65)	0 90 (−10.68)	30–40	
(66)[f,g]	22				17	

Table I (continued)

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[a]1: 6-31G*//6-31G*: ref. 9a, b; 2: 6-31G//6-31G: ref. 9d; 3–5: STO-3G, rigid rotor approx.: ref. 9e; 7, 8: STO-3G, ref. 9g; 9: STO-3G: ref. 9h; 10–14: STO-3G, rigid rotor: ref. 9i; 15–20: STO-3G, rigid rotor: ref. 9j; 22–25: STO-3G, rigid rotor: ref. 9k; 34: STO-3G//MNDO: ref. 4c; 35–37: STO-3G: ref. 6h; 38: STO-3G: ref. 91; 39–41; STO-3G: ref. 9m; 42,43: STO-3G: refs. 9a,n; 44: STO-3G: ref. 9a; 45: STO-3G: ref. 9o; 46: STO-3G: ref. 9p; 47–53: STO-3G ref. 9q; 54,55: STO-3G: ref. 9t; 56,57: STO-3G: ref. 9r; 65: STO-3G: ref. 9s;

[b]1:Raman spectra: ref. 10a; 2: SVL-fluorescence: ref. 10d; 3: NMR: ref. 10y; 5: microwave spectra: ref. 10w; 6: ^{13}C-NMR: ref. 4f; 7,8: electron diffraction: refs. 10e,f; 9: electron diffraction: ref. 10g; 10,11: Kerr constants: ref. 10i; 10,12: NMR: ref. 10j; 11,15: dipole moments: ref. 10l; 15,20: PES: ref. 10k; 16: dielectric relaxation: ref. 10m; 20: NMR: ref. 10z; 22: NMR: ref. 10n, electron diffraction: ref. 10o; 26,27: UV: ref. 10p; 28,31,32: [13]C: ref. 10q; 28: PES: ref. 5d; 33: dipole moments, Kerr constants: ref. 10s; 35: IR: ref. 10t, NMR: ref. 10u; 38: PES: ref. 10v; 39: X-ray: ref. 10x; 42: Raman spectra: ref. 11a; 43: IR, microwave spectra: ref. 9n; 44: microwave spectra: refs. 11b,c; 45: far-IR: ref. 11d; 46: X-ray: ref. 11e; 47,51–53: gas-phase IR: ref. 11f; 48: NMR,IR: refs. 11q,r; 49: microwave spectra: ref. 11j; 50: NMR: ref. 11k; 54,55: estimated from correlations of ^{17}O-NMR shifts with MM2 torsional angles: ref. 6e; 55: dipole moment, Kerr constant: ref. 11m; 56: microwave spectra: ref. 11n; 57: Raman spectra: ref. 10h; 58,59: ^{17}O-NMR: ref. 6f; 65: MCD spectra: ref. 11o; 66: X-ray: ref. 11p.

[c]For AM1 results see also ref. 4d.

[d]AM1 minima and barriers obtained by drawing a smooth curve through the calculated points. For benzophenone no reasonable fit of the AM1 results to a six-term Fourier series was possible (as was the case with *ab initio* calculations 9p).

[e]For AM1 results see also ref. 4b.

[f]CA nomenclature: 33: 1-phenyl-1H-pyrrole-2,5-dione; 34: 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione; 66: 1-phenyl-4,5-dihydro-3,3-dimethyl-5-oxo-3H-1,2,4-triazolium cation.

[g]Minimum obtained by optimization of the dihedral angle.

[h]IR: cisoid conformation; NMR: either highly twisted or nearly free rotation: ref. 12.

10–15°)[10b, c]. In contrast, slight deviations from planarity are predicted by AM1 for styrene **2** and 4-vinylpyridine **5**, whereas *ab initio* calculations[9d–f] as well as experimental results[10d, w] indicate a planar conformation for both compounds. Through a rather large range of θ ($\approx$ 20°), however, the potential energy curve is extremely flat and only a very small change in the experimental values of V_2 and V_4 [cf. eq. (1)] could have given $\theta_{min} >$ 0°.[9d, 10d] In any case, the barriers to planarity predicted by AM1 (**2**: 0.4 kJ mol^{-1}, **5**: 0.1 kJ/ mol) are very low and both molecules, therefore, may be viewed as effectively planar. Less satisfactory are the AM1 results for 2-vinylpyridine **3**. Although in agreement with both experiment[10y] and *ab initio* calculations,[9e] AM1 predicts the Z conformation as the more stable one, a rather large dihedral angle is obtained for the second stable rotamer. As will become more evident later this seems to be due to an overestimation of the repulsion between the nitrogen lone pair and the Cα-hydrogen atom. For compounds **4** and **6–9** the equilibrium twist angles obtained by AM1 are in excellent agreement

with *ab initio* and/or experimental results. The above mentioned overestimation of nitrogen lone pair — *ortho*-hydrogen repulsions is well documented in the series of azabiphenyls **10–25**. Within this series five types of sterical interactions may be distinguished: (i) only hydrogen atoms are present in the ortho positions of the two rings linked by an essential single bond (compounds **11, 14, 18–20**, and **25**). Here the AM1 results compare quite favorably with *ab initio* as well as experimental data. In fact, AM1 predicts even slightly less twisting than do *ab initio* computations (Table I). The same also holds for biphenyl **9** itself. (ii) One of the hydrogen–hydrogen interactions is replaced by a nitrogen lone pair–hydrogen interaction (**10, 13, 16, 17**, and **24**). For these compounds AM1 also yields quite acceptable results but now a somewhat larger twisting as compared to *ab initio* results is obtained. (iii) For compounds with two hydrogen–nitrogen lone pair interactions (**12**, (*E*)-**15**, (*E*)-**23**) AM1 already yields unreasonable results (error in $\theta_{min} >$ 30°). (iv) One lone pair–lone pair and consequently one hydrogen–hydrogen

[(Z)-15, (Z)-23] or one hydrogen–lone pair (21) interaction: in contrast to *ab initio* calculations, only marginal stabilities with respect to the central barrier ($\delta E < 0.5$ kJ/mol) are obtained by AM1. (v) For 2,2'-bipyrimidine 22 with two lone pair–lone pair repulsions AM1 completely is in error (see Table I). From *ab initio* computations on the azabiphenyls a decrease of steric repulsions in the order H–H > lone pair–lone pair ≫ lone pair–H has been suggested.[15] From the results presented above, this sequence for AM1 reads as lone pair–lone pair > lone pair–H > H–H. Thus we conclude that in AM1 the overestimation of H–H repulsions present in MNDO has been largely corrected. In contrast, lone pair–H and even more pronounced lone pair–lone pair repulsions are still overestimated in AM1. Thus, for compounds having these structural features AM1 should be used with some caution. For compounds 26–43, 45–50, 52–59, 65, and 66, the AM1 results are in good to excellent agreement with *ab initio* and/or experimental data and need not be discussed further here. The AM1 results for glyoxal 44 and pyridine-2-carboxaldehyde 51 are taken as additional evidence for the previously discussed overestimation by AM1 of repulsions between lone pairs. For glyoxal, AM1 finds no second minimum. In fact, the Z conformation is, in sharp contrast to both experiment as well as *ab initio* computations, found to be a transition state (one negative eigenvalue of the force constant matrix) rather than a minimum. In the case of pyridine-2-carboxaldehyde, AM1 finds a much too large twist angle (42° vs. 0°) as compared to *ab initio* calculations as well as only marginal stability for the cisoid conformation. However, it should be noted that experimentally besides the stable E isomer, no indication for a second rotamer could be detected.[11s] Pending further experimental evidence thus, it remains unclear whether this second rotamer indeed corresponds to a stable minimum as suggested by *ab initio* calculations. Similarly, for 52 experimental information seems to be available only for the more stable E isomer.[11l] The conformational properties of the cationic systems 60–64 will be discussed below with respect to their chemical reactivity.[4a] In order to rationalize the preferred orientation (meta vs. para)

in electrophilic substitution reactions observed experimentally in these compounds in ref. 4a FMO-type reactivity indices fm and fp for meta and para substitution, respectively, based on MNDO computations were used. In complete agreement with experimental results for 60, a strong preference for meta substitution independent of the torsional angle was predicted on this basis.[4a] However, for compounds 61–64, it was necessary to assume probable interannular angles to obtain agreement with the experimentally observed position of substitution (MNDO consistently yields $\theta_{min} \approx 90°$ for these compounds).[4a] Here we use the very same approach. Like MNDO, for 60 AM1 yields fm > fp for all dihedral angles θ in agreement with experimental findings. The results for compounds 61–64 (plots of δE, fm, and fp vs. θ) are shown in Figure 1 (to be compared to Fig. 1 of ref. 4a). In complete agreement with experiment[4a] at θ_{min}, thus preferred para substitution for 61 and 64 (Figs. 1a and 1d) and meta substitution for 62 (Fig. 1b) is predicted by AM1. Therefore, no *ad hoc* assumption of a reasonable torsional angle is necessary for these compounds. Only for 63 disagreement with experiment is found.

Rotational Barriers

In contrast to dihedral angles the performance of AM1 with respect to the calculation of rotational barriers is much less satisfactory. Even if one admits that *ab initio* methods tend to overestimate conjugative interactions, and consequently, barriers to rotation (cf. the data of Table I and refs. 9d, n, q, and 15), the results of Table I clearly indicate that AM1 greatly underestimates rotational barriers around essential single bonds. Compared to *ab initio* and the few available experimental data, AM1 barriers are too low by 50% and even more. The best one can hope here is that at least general trends within a series of structurally related compounds will be correctly reproduced by AM1. However, the data for the azabiphenyls 10–25 or the isomeric bifurans 35–37 seem to indicate that even trends are not correctly described. Thus great care is necessary in the use of AM1 for the computation of rotational barriers around single bonds in conjugated molecules.
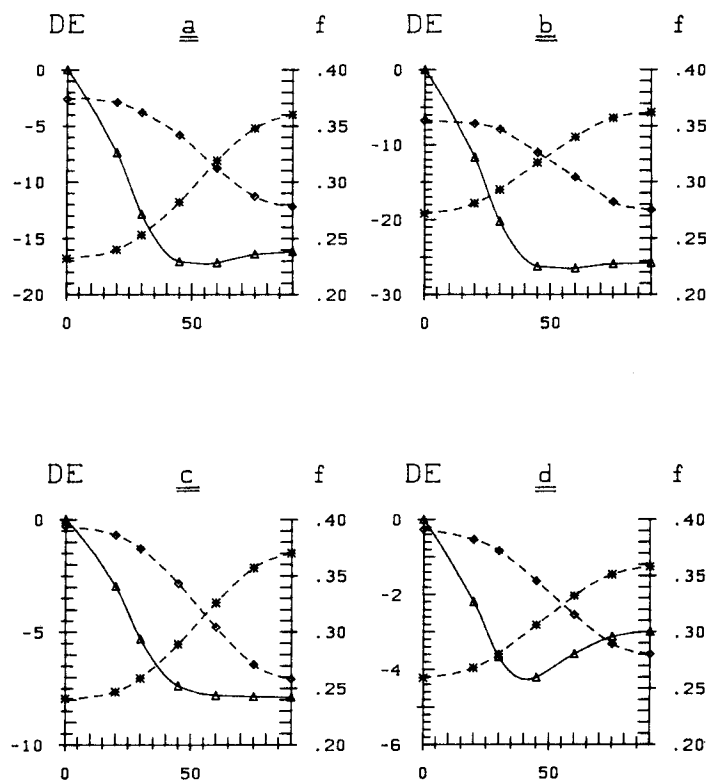
Figure 1. Plots of δE ($\triangle$), f_m (*), and f_p ($\diamond$) versus the dihedral angle θ for (a) compound **61**, (b) compound **62**, (c) compound **63**, and (d) compound **64**.

E/Z Energy Differences

Although in a number of cases much too low (e.g., **1, 15, 23, 39, 42**) E/Z energy differences are obtained by AM1 (as also is the case with ab initio calculations,[9a,b,n]), the preferred conformations for almost all compounds capable of E/Z isomerism is correctly predicted by this semiempirical method. The only exceptions are 2,2′-bifuran **35**, methacrolein **43**, and the previously discussed glyoxal **44**. However, experimental results concerning the preferred conformation of **35** is contradictory, favoring either the Z conformation[10t] (as does AM1) or the E conformation[10u] (as do ab initio calculations[6h]). For furan- as well as pyrrole-3-carboxaldehyde (**48** and **50**), both AM1 and STO-3G[9q] predict the Z conformation to be more stable in contrast to experimental evidence.[11k,q,r] However, the conformational behavior of these compounds is strongly affected by the medium.[11g–i] Lacking gas-phase experiments, no resolution to these discrepancies is possible. In general, however, AM1 can be expected to give at least correct trends for E/Z energy differences.

Ionization Potentials

HOMO energies obtained by AM1 are listed in Table II and compared to experimental ionization potentials and/or STO-3G orbital energies. Although the calculated ionization potentials are generally too high (error <0.5 eV) with a few exceptions (e.g., acrolein **42** and glyoxal **44**) AM1 picks up trends quite nicely (correlation coefficients: AM1 (29 data points): $r = 0.969$: STO-3G (22 data points): $r = 0.810$). So, for example, the experimentally found sequence for the first ionization potential of hydrocarbon species (**8** < **7** < **9** < **2** < **1**) as well as biphenyl derivatives (**9** < **15** < **16** < **17** < **25** < **20** < **24** < **23**) is completely in agreement with the AM1 predictions. Thus AM1 appears to be a quite reliable method for the calculation of ionization potentials.

V. CONCLUSIONS

It seems clear from the above discussion that despite some remaining weaknesses (i.e., overestimation of lone pair–lone pair repulsions), AM1 represents a very real im-

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Table II. Comparison of AM1 and STO-3G HOMO energies with experimental ionization potentials (in eV).

| | $-\varepsilon$(HOMO) | | | | $-\varepsilon$(HOMO) | | |
	AM1	STO-3G[a]	IP[b]		AM1	STO-3G[a]	IP[b]
1	9.33	7.07	9.07	28	8.77		8.16
2	9.03	6.57	8.47	35	8.51	5.94	
3	9.23	7.17	8.92	36	8.58	6.14	
4	9.26	7.31		37	8.77	6.37	
5	9.71	7.63	9.25	38	9.03	6.74	8.30
7	8.80		8.17	39	7.86	5.08	
8	8.58		7.87	40	7.75	5.07	
9	8.94	6.54	8.27	41	7.75	5.22	
10	9.15	6.81	8.51	42	10.69	8.60	10.10
11	9.42	7.07	9.01	44	10.66	9.11	10.59
15	9.32	7.01	8.60	45	10.00		9.52
16	9.36	7.23	8.81	46	9.87		9.40
17	9.68	7.48	9.59	47	9.74		9.21
18	9.35	7.23		51	10.23	8.18	9.75
19	9.67	7.54		53	10.25	8.42	10.12
20	10.06	7.91	9.75	54	10.08	7.62	9.73
23	10.31	8.34	9.86	55	9.95		9.40
24	10.10	8.20	9.77	57	10.56	10.98	9.92
25	9.87	8.17	9.68	58	11.35	12.01	10.65

[a] 1,2,42: ref. 17a; 3–5: ref. 9e; 9–11,18: ref. 5b; 15–17,19,20: ref. 9j; 23–25: ref. 9k; 35–37: ref. 17b; 38: ref. 91; 39–41: ref. 9m; 51,53: ref. 17c; 54: ref. 17d; 57,58: ref. 17e.

[b] 1,2,9,42,45,46,47,51,53–55,57: ref. 18a; 7,8: ref. 18b; 10,11: ref. 5b; 15–17,20: ref. 9j; 23–25: ref. 9k; 28: ref. 5d; 38: ref. 10v; 44: ref. 3; 58: ref. 17e.

provement over MNDO with respect to conformational problems in conjugated molecules. Furthermore, for compounds capable of E/Z isomerism, AM1 generally yields correct predictions of conformational preferences. Energy differences between the conformers are, however, usually considerably too low. If used with some caution AM1 thus should prove a rather useful yet inexpensive tool for studying this type of problem. It is hoped that the compilation presented herein will serve as guidelines to when AM1 can be applied with confidence. For the calculation of rotational barriers we do not recommend AM1. With respect to trends in first ionization potentials AM1 performs quite successfully.

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