Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XII. Conformations, Stabilities, and Charge Distributions in Monosubstituted Benzenes

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Abstract: *Ab initio* molecular orbital theory with the minimal STO-3G basis set is used to study the conformations, stabilities, and charge distributions of 35 monosubstituted benzenes. Molecular conformations are found to be largely determined by conjugation effects, although steric interactions cause significant perturbations in some cases. Rotational barriers are a little higher than experimental values. In the most stable forms of these molecules, the phenyl group is stabilizing compared with methyl. On the other hand, a phenyl group oriented *perpendicular* to the π system of the substituent (*e.g.*, the orthogonal forms of nitrobenzene and benzaldehyde) is often destabilizing. Calculated dipole moments are consistently lower than experimental values, but most experimental trends are reproduced. In particular, calculated and experimental mesomeric moments are in close agreement. Theoretical charge distributions support many of the ideas of classical organic chemistry. However, in addition to the *transfer* of π electrons to or from the substituent into the aromatic ring, *polarization* of the π electrons within the ring is important. Charge distributions in orthogonal conformations can be strikingly different from those in corresponding planar forms.

The interaction of a substituent with a benzene ring is of great importance in determining the structures and stabilities of many organic molecules. Early theoretical work on this topic[1] was mainly concerned with π-type interactions between the substituent and the aromatic system and took little account of the σ-electron effects which may also influence the conformation and energy of interaction. Some semiempirical studies taking account of all valence electrons have been published,[2] leading to a moderately successful description of the polarity of such molecules. The aim of the present paper is to make a fuller theoretical study of monosubstituted benzenes using *ab initio* molecular orbital theory.

Three aspects of this subject are investigated in detail. In the first place, we shall be concerned with the determination of the most stable conformations of the substituted benzenes and with the associated barriers to internal rotation. This will be accomplished by a series of calculations using a standard geometrical model for bond lengths and angles proposed previously.[2a] In some rotamers, of course, the use of a standard model leads to strong steric repulsions. To make some allowance for this, a limited number of calculations have been made in which one bond angle is allowed to change until the energy is minimized. A similar partial allowance for the effects of steric interaction was found to give a reasonable description of C_3 and C_4 hydrocarbons in a previous study.[3]

The second aim of the work is to investigate the stabilizing effect of the substituent X on the benzene ring. This is done by examining the theoretical energies for the formal reaction

$$C_6H_5X + CH_4 \longrightarrow C_6H_6 + CH_3X \qquad (1)$$

and comparing with experimental values where possible, standard geometries being used for CH_4, C_6H_6, and CH_3X. The energy of reaction 1 compares the effect of the substituent X on the stability of the benzene substrate with its effect on the stability of methane and is thus a measure of the relative stabilization of benzene by a substitutent X. For the sake of brevity, we shall refer to energies of reaction 1 as *stabilization energies*. This reaction is *isodesmic* (formal bond types are conserved), and previous work has suggested that the energies of such reactions are quite well given by reasonably simple levels of molecular orbital theory.[4-6]

Finally, we shall make a study of the charge distributions and dipole moments in this set of molecules. This supplements and extends previous work.[7]

Methods

The methods used have been introduced in previous publications and will not be described here in full detail. The molecular orbital method is single-determinant self-consistent theory based on the Roothaan equations.[8] The basis set is minimal STO-3G, which consists of linear combinations of three Gaussian functions which are least-squares fitted to exponential Slater-type atomic orbitals.[9] Standard molecular exponents proposed previously are used.

Unless otherwise specified, the geometry used for bond lengths and angles is the standard model proposed in part I of this series.[2a] This leaves dihedral angles (angles measuring internal rotation) unspecified. Here a staggered arrangement is always used for bonds connecting two atoms with tetrahedral bond angles. For the bond connecting the substituent to the benzene ring, a variety of dihedral arrangements have been con-

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[1] See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

[2] See, for example, (a) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); (b) N. C. Baird and M. J. S. Dewar, *Theor. Chim. Acta*, **9**, 1 (1967); (c) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968). For a recent review, see (d) G. Klopman and B. O'Leary, *Fortsch. Chem. Forsch.*, **15**, 445 (1970).

[3] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

[4] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *ibid.*, **92**, 4796 (1970).

[5] L. Radom, W. J. Hehre, and J. A. Pople, *ibid*, **93**, 289 (1971).

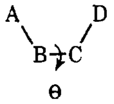
[6] L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).

[7] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970).

[8] C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[9] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

sidered. For a nonlinear arrangement of four atoms



θ = 0 shown

we use the terms *cis*, *orthogonal*, and *trans* for $\theta = 0$, 90, and 180°, respectively.

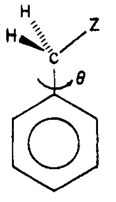
As noted in the introduction, we have permitted bond angle deviations from the standard model in certain molecules in order to allow for steric repulsions. These relaxations will be described in the appropriate parts of the next section.

The lowest theoretical energy for each molecule is then used to calculate the energy of reaction 1 and is compared with experimental values derived from available heats of formation. In addition, we report theoretical electron populations[10] and expectation values of dipole moments derived from the wave functions by standard methods.

Results and Discussion

Some of the results of the computations carried out are given in Tables I–III and Chart I. Table I lists the total and relative energies for various conformations of the substituted benzenes. Table II contains some previously unpublished results for substituted methanes which are required to calculate the energies of reaction 1.[11] These energies are compared with experiment in Table III, which also includes calculated charges and dipole moments. Calculated π-electron populations are given in Chart I. We shall discuss the results for groups of molecules in turn.

Toluene and Related Molecules. We first consider toluene and substituted molecules $C_6H_5CH_2Z$ ($Z = CH_3, NH_2, OH, F$). Rotation about the bond to phenyl



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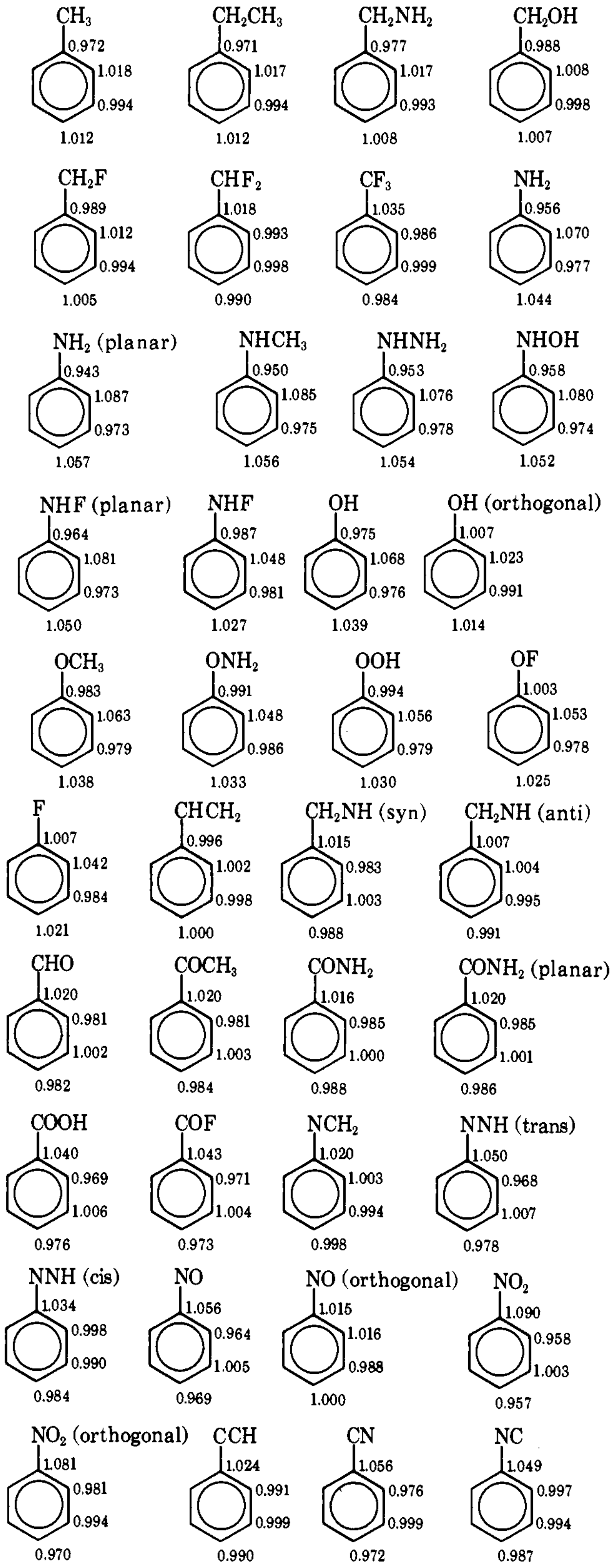
will generally lead to a twofold barrier. For toluene itself, the barrier is sixfold. According to computations on the cis ($\theta = 0$) and orthogonal ($\theta = 90°$) form, the barrier is less than 10^{-5} hartree (6 cal mol^{-1}) and probably below the level of significance of the calculations. However, it should be noted that bond angle relaxation was not permitted during rotation, probably leading to underestimation of the sixfold barrier. (This was found to be so in the rather similar problem of methyl rotation in the ethyl cation.[12,13]) Experimentally, a rotation barrier of 14 cal mol^{-1} is reported,[14] but the lowest energy conformation is unknown.

For ethylbenzene a staggered arrangement about the CH_2CH_3 bond was assumed. If standard bond angles are used, the most stable structure is found to be the orthogonal form ($\theta = 90°$) with a rotational barrier of 4.7 kcal mol^{-1}. However, this is probably an overestimate, since the cis form ($\theta = 0$) leads to some steric interference between the methyl group and one of the ortho hydrogens, so further computations were carried out allowing for optimization with respect to

Chart I. π-Electron Populations in Substituted Benzenes[a]



[a] Unless otherwise specified, values given are for the lowest energy conformations listed in Table I. For unsymmetrical molecules, electron populations shown at the ortho and meta positions are average (ortho–ortho′ and meta–meta′, respectively) values.

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(10) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(11) All remaining energies for substituted methanes required for the calculations in this paper may be found in ref 6.

(12) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970).

(13) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).

(14) H. D. Rudolph, H. Dreizler, A. Jaeschke, and P. Windling, *Z. Naturforsch. A*, **22**, 940 (1967).

Table I. Energy Data for Monosubstituted Benzenes

Molecule (C_6H_5–X)	Substituent (X)	Conformation[a,b]	Total energy, hartrees	Relative energy,[c] kcal mol^{-1}	$\Delta H_f°$(298°),[d] kcal mol^{-1}
Benzene	-H		−227.89006		19.82
Toluene	$-CH_3$	CCCH cis	−266.47382	0	11.95
		CCCH orthogonal	−266.47382	0.00	
Ethylbenzene	$-CH_2CH_3$	CCCC orthogonal, CCC = 112.0°	−305.05387	0	7.12
		CCCC orthogonal	−305.05333	0.34	
		CCCC cis, CCC = 115.1°	−305.04999	2.43	
		CCCC cis	−305.04588	5.01	
Benzylamine	$-CH_2NH_2$	CCCN orthogonal, CCN: trans	−320.77980	0	
		CCCN orthogonal, HCN: trans	−320.77924	0.35	
		CCCN cis, HCN: trans	−320.77623	2.24	
		CCCN cis, CCN: trans	−320.77334	4.05	
Benzyl alcohol	$-CH_2OH$	CCCO cis, CCOH trans	−340.29628	0	−22.5
		CCCO orthogonal, HCOH trans	−340.29618	0.06	
		CCCO orthogonal, CCOH trans	−340.29593	0.22	
		CCCO cis, HCOH trans	−340.29322	1.92	
Benzyl fluoride	$-CH_2F$	CCCF cis	−363.91885	0	
		CCCF orthogonal	−363.91845	0.25	
Benzal fluoride	$-CHF_2$	CCCH cis	−461.38023	0	
		CCCH orthogonal	−461.37995	0.18	
Trifluoromethylbenzene	$-CF_3$	CCCF cis	−558.85457		−143.42[e]
Aniline	$-NH_2$	Pyramidal N (HNH = 112.1°)	−282.20892	0	20.8
		Planar	−282.20458	2.72	
N-Methylaniline	$-NHCH_3$	CNCH trans	−320.78039	0	21.6
		CNCH cis	−320.77143	5.62	
Phenylhydrazine	$-NHNH_2$	CNN: cis	−336.49381	0	50.1
		CNN: trans	−336.49298	0.52	
N-Phenylhydroxylamine	-NHOH	CNOH orthogonal	−355.99863	0	
		CNOH trans	−355.98517	8.45	
		CNOH cis	−355.97897	12.34	
N-Fluoroaniline	-NHF	Pyramidal N (HNF = 109.5°)	−379.62218	0	
		Planar	−379.61088	7.1	
Phenol	-OH	CCOH cis	−301.72861	0	−23.1
		CCOH orthogonal	−301.72039	5.15	
Anisole	$-OCH_3$	CCOC cis, COC = 118.0°	−340.30429	0	−18.0
		CCOC orthogonal, COC = 111.7°	−340.30420	0.06	
		CCOC orthogonal	−340.30393	0.23	
		CCOC cis	−340.29630	5.01	
O-Phenylhydroxylamine	$-ONH_2$	CON: cis	−356.00885	0	
		CON: trans	−355.99699	7.44	
Phenyl hydroperoxide	-OOH	CCOO cis, COOH orthogonal	−375.50808		
Phenyl hypofluorite	-OF	CCOF cis	−399.12807		
Fluorobenzene	-F		−325.34939		−27.86[e]
Styrene	$-CHCH_2$	CCCC cis, CCC = 128.0°	−303.82979	0	35.22
		CCCC cis	−303.82479	3.14	
		CCCC orthogonal, CCC = 124.7°	−303.82275	4.42	
		CCCC orthogonal	−303.82176	5.04	
syn-Benzaldimine	-CHNH	CCCN cis, HCNH cis	−319.57835		
anti-Benzaldimine	-CHNH	CCCN cis, HCNH trans	−319.56998		
Benzaldehyde	-CHO	CCCO cis	−339.11540	0	−6.0
		CCCO orthogonal	−339.10489	6.60	
Acetophenone	$-COCH_3$	CCCO cis	−377.70219	0	−20.76[f]
		CCCO orthogonal	−377.69520	4.39	
Benzamide	$-CONH_2$	CCCO 30°	−393.43220	0	
		CCCO cis	−393.43094	0.79	
		CCCO orthogonal	−393.42759	2.89	
Benzoic acid	-COOH	CCCO cis, CCOH trans	−412.97347	0	−69.36[f]
		CCCO orthogonal, CCOH trans	−412.96429	5.76	
		CCCO cis, CCOH cis	−412.96245	6.92	
Benzoyl fluoride	-COF	CCCO cis	−436.59036		
N-Phenylformaldimine	$-NCH_2$	CCNC cis	−319.54070		
trans-Phenyldiimide	-NNH	CCNN cis, CNNH trans	−335.30244		
cis-Phenyldiimide	-NNH	CCNN cis, CNNH cis	−335.26214		
Nitrosobenzene	-NO	CCNO cis	−354.81588	0	
		CCNO orthogonal	−354.80816	4.84	
Nitrobenzene	$-NO_2$	CCNO cis	−428.58323	0	
		CCNO orthogonal	−428.57408	5.74	
Phenylacetylene	-CCH		−302.61970		78.22[f]
Benzonitrile	-CN		−318.44330	52	52.3
Phenyl isocyanide	-NC		−318.40890		

[a] Conformations are described from left to right across the molecular skeleton. [b] N: refers to the fourth tetrahedral direction for pyramidal nitrogen. [c] Energies relative to that of the minimum-energy conformation for the particular molecule. [d] Data used to obtain experimental energies for reaction 1, unless otherwise specified, from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [e] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). [f] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

Table II. Energy Data for Substituted Methanes[a]

Molecule	Conformation	Energy, hartrees	$\Delta H_f°(298°)$,[b] kcal mol^{-1}
1,1-Difluoroethane	Staggered	−273.21460	−118.0[c]
1,1,1-Trifluoroethane	Staggered	−370.68983	−178.2[c]
Acetone	HCCO cis, OCCH cis	−189.53389	−51.7
Acetamide	HCCO cis	−205.26598	−57.8
Acetic acid	HCCO cis, CCOH trans	−224.80290	−103.8
Acetyl fluoride	HCCO cis	−248.41978	−104.9[d]
Nitromethane	HCNO orthogonal	−240.41548	−17.9

[a] Energies for other substituted methanes required in this paper are from ref 6. [b] Unless otherwise specified, from the reference of footnote *d*, Table I. [c] See footnote *e*, Table I. [d] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, W. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

Table III. Stabilization Energies, Electric Dipole Moments, and Mulliken Charges for Substituted Benzenes (Ph–X)

	Stabilization energy,[a,b] kcal mol^{-1}		Dipole moment, D				
Molecule (PhX)	Calcd	Exptl[c]	Calcd	Exptl[d]	q_σ[e]	q_π[e]	$\pi_{\mathrm{Ph-X}}$[f]
PhH	0	0	0	0	−0.063	0	0
PhCH$_3$	3.1	5.5	0.25	0.36	−0.007	−0.008	0.009
PhCH$_2$CH$_3$	3.4	5.8	0.28	0.59	−0.013	−0.005	0.013
PhCH$_2$NH$_2$	2.6		1.32	1.31	−0.024	−0.005	0.015
PhCH$_2$OH	2.2	4.0	1.37	1.71	+0.002	−0.007	0.009
PhCH$_2$F	2.1		1.02	1.77	+0.003	−0.006	0.008
PhCHF$_2$	1.2		1.48		+0.009	+0.010	0.018
PhCF$_3$	0.9	2.9	1.67	2.86	+0.021	+0.011	0.017
PhNH$_2$ (pyramidal N)	9.7	11.4	1.44	1.53	+0.140	−0.095	0.048
PhNH$_2$ (planar)	7.0		1.30		+0.159	−0.120	0.063
PhNHCH$_3$	4.9	11.7	1.41	1.67	+0.157	−0.126	0.069
PhNHNH$_2$	3.6	10.2	2.54	1.67	+0.175	−0.116	0.060
PhNHOH	1.1		1.72		+0.175	−0.119	0.062
PhNHF (planar)	−1.7		1.04		+0.192	−0.122	0.061
PhNHF (pyramidal N)	5.4		1.41		+0.157	−0.073	0.039
PhOH	12.4	12.9	1.22	1.45	+0.185	−0.102	0.052
PhOCH$_3$	5.5	11.7	1.22	1.38	+0.192	−0.105	0.057
PhONH$_2$	4.7		1.30		+0.206	−0.092	0.045
PhOOH	5.5		1.73		+0.205	−0.094	0.047
PhOF	5.9		1.23		+0.226	−0.090	0.044
PhF	11.4	9.6	0.93	1.60	+0.215	−0.080	0.038
PhCHCH$_2$	6.1	7.4	0.11	0	+0.003	+0.006	0.053
PhCHNH (syn)	6.5		1.62		+0.017	+0.025	0.053
PhCHNH (anti)	2.4		2.44		+0.004	+0.016	0.053
PhCHO	5.3	4.0	1.90	2.98	−0.001	+0.032	0.047
PhCOCH$_3$	3.1	6.8	1.95	3.02	−0.007	+0.028	0.047
PhCONH$_2$	1.8		2.81	3.77	+0.004	+0.020	0.035
PhCONH$_2$ (planar)	1.0		2.74		+0.005	+0.022	0.041
PhCOOH	4.5	3.3	1.08	1.72	+0.029	+0.034	0.044
PhCOF	4.5		2.49		+0.025	+0.036	0.045
PhNCH$_2$	(−13.7)[g]		1.77		+0.108	−0.012	0.053
PhNNH (trans)	1.7		0.56		+0.132	+0.022	0.050
PhNNH (cis)	(−14.8)[g]		3.62		+0.123	+0.006	0.052
PhNO	2.9		2.38	3.17	+0.110	+0.037	0.054
PhNO$_2$	2.8		4.26	4.22	+0.227	+0.031	0.034
PhCCH	6.8	3.8	0.52	0.73	+0.058	+0.005	0.047
PhCN	5.8	6.3	3.65	4.18	+0.104	+0.022	0.043
PhNC	8.3		3.17	3.56	+0.240	−0.018	0.035

[a] This is the energy for the reaction $\mathrm{PhX + CH_4 \rightarrow PhH + CH_3X}$. [b] Calculated from data in Tables I and II and ref 6. [c] Calculated from experimental $\Delta H_f°(298°)$ values without any temperature or vibrational corrections. [d] From ref 22. [e] q_σ and q_π are the total σ and π charges, respectively, donated to the ring by the substituent X. [f] $\pi_{\mathrm{Ph-X}}$ is the Mulliken overlap population of the adjacent π-type p orbitals in the bond joining X to the ring. [g] These values are not significant because of large uncorrected steric effects.

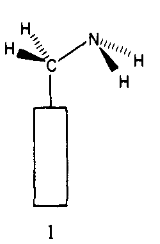
the CCC angle in the ethyl group. This was done both for the cis and orthogonal arrangement. In this variation, the hydrogens of the methylene group were moved so that the CCH angles remained tetrahedral. It was found that the CCC angle opened for both conformations, but by the larger amount (to 115.1°) for the cis form. The calculated barrier is reduced by this procedure to 2.2 kcal mol^{-1}, the orthogonal form still being the more stable. A thermodynamic estimate[15] of the barrier in ethylbenzene is 1.3 kcal mol^{-1}.

(15) F. G. Brickwedde, M. Moskow, and R. B. Scott, *J. Chem. Phys.*, 13, 547 (1945).

It is difficult to determine whether the predicted orthogonal C_s form for ethylbenzene is due entirely to the steric distortion in the planar form or whether there is a more favorable hyperconjugative interaction with the benzene π electrons in the orthogonal arrangement. We may note that comparable calculations on the 1-propyl cation (which may be considered as an ethyl group attached to a trigonal sp^2 carbonium center) lead to a similar orthogonal structure and twofold barrier.[16,17] Since there is little steric interaction in this cation, this result suggests than any stabilization due to C–C hyperconjugation is stronger than that due to C–H hyperconjugation. However, the total hyperconjugative interaction is much stronger in the 1-propyl cation, and the corresponding differences should be smaller in a neutral molecule. Another similar calculation can be carried out on nitroethane, where steric interaction is also likely to be small. Using the standard model, the STO-3G basis predicts the orthogonal form of nitroethane to be more stable than the cis form, but only by 0.7 kcal mol^{-1}. It therefore seems likely that both steric and hyperconjugative interactions influence the barrier in ethylbenzene.

Although there is no direct experimental evidence on the structure of ethylbenzene, crystal structures of some related molecules are reasonably consistent with the predicted orthogonal configuration. Thus both β-phenylethylamine hydrochloride[18] and bibenzyl[19] have CCCC dihedral angles (corresponding to θ) close to 70°.

For benzylamine and benzyl alcohol, consideration must also be given to rotation about the C–Z bond. Here again, we have assumed a staggered arrangement. For benzylamine, the orthogonal form I ($\theta = 90°$) is found to be more stable, with the NH_2 group symmetrically arranged to give an overall C_s symmetry. Benzyl alcohol and benzyl fluoride, on the other hand, have slightly lower theoretical energies in the cis ($\theta = 0$) forms, with C–Z and the phenyl ring coplanar (II and III). Benzal fluoride has its lowest energy in the cis hydrogen form IV. However, for these latter three molecules, the rotational barriers are only of the order of 0.2 kcal mol^{-1}. The full set of results suggests that for ethylbenzene and benzylamine the orthogonal form has lower energy because of some steric repulsion in the cis form, but this source of rotational barrier is not present in benzyl alcohol, benzyl fluoride, and benzal fluoride, where the structures II–IV avoid such interactions. The cis forms of benzyl alcohol and benzyl fluoride could be more stable than the orthogonal forms partly because of hyperconjugation effects. Calculations on the 2-hydroxyethyl and 2-fluoroethyl cations[20] give lowest energy conformations analogous to II and III and suggest that C–O and C–F hyperconjugation are less effective in lowering the energy than C–H hyperconjugation.



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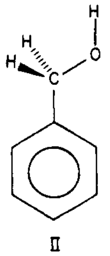

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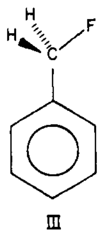

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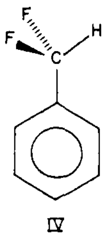
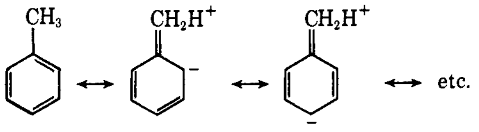


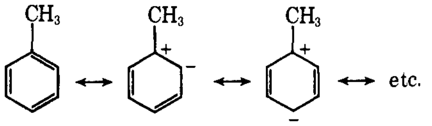
IV

For all the substituted toluenes, the stabilization energies (listed in Table III) are positive. The theoretical value for toluene (3.1 kcal mol^{-1}) is somewhat less than the experimental value (5.5 kcal mol^{-1}). Ethylbenzene and toluene have nearly equal values. However, the stabilizing effect of the substituent is apparently reduced when electronegative groups are attached to the methyl group of toluene. This is borne out by the experimental results, such as the relatively low value for trifluoromethylbenzene.

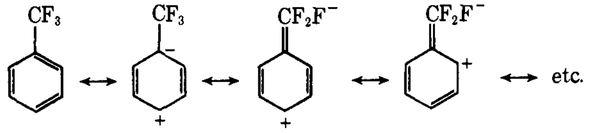
The charge distributions in these molecules show a number of significant features. Toluene is found to have a small dipole moment (0.25 D) in the direction Me^+–Ph^-, in agreement with experimental data.[21,22] This arises primarily from a polarization of the π electrons (Chart I) leading to an alternating π charge in the ring with negative charges at the ortho and para positions. This is compatible with valence structures commonly drawn for toluene.



However, π donation from methyl to phenyl is smal (0.008), suggesting that structures involving *polarization* (as opposed to *transfer*) of π electrons in the aromatic ring are also important. These results are very similar to those of previous calculations[7] using optimized molecular exponents.



As the methyl is substituted with electronegative groups, this effect is reduced. In trifluoromethylbenzene, the charge alternation is reversed (ortho and para positions positive) and there is a small π-electron withdrawal from the ring (0.011).



The calculated dipole moment of trifluoromethylbenzene (1.67 D) is larger than that of typical[23] aliphatic

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[16] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970).

[17] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6987 (1970).

[18] G. Tsoucaris, *Acta Crystallogr.*, **14**, 909 (1961).

[19] D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949).

[20] (a) L. Radom, J. A. Pople, and P. v. R. Schleyer, to be published; (b) D. T. Clark and D. M. J. Lilley, *J. Chem. Soc. D*, 603 (1970).

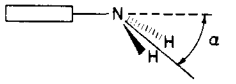
[21] See, for example, the dipole moments of substituted toluenes in ref 22.

[22] (a) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963; (b) R. D. Nelson, D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase," NSRDS-NBS 10, U. S. Government Printing Office, Washington, D. C., 1967.

[23] It is best to compare the dipole moments of molecules C_6H_5–X with *tert*-Bu–X to obtain mesomeric moments (see, for example, L. E. Sutton in "Determination of Organic Structures by Physical Methods," Vol. I., E. A. Braude and F. C. Nachod, Ed., Academic Press, New

trifluoromethyl derivatives (*e.g.*, μ(calcd) for CH_3CF_3 is 1.34 D), in agreement with experiment[24] (2.86 D *vs.* 2.32 D). These values indicate a mesomeric component in trifluoromethylbenzene of about 0.3 D in the opposite direction ($Ph^+{-}CF_3^-$) to that in toluene. Charge distributions in the other compounds lie between these extremes.

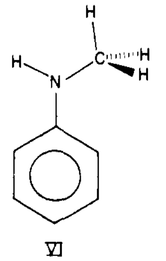
Aniline and Related Molecules. We next consider aniline and N-substituted derivatives, C_6H_5NHZ (Z = CH_3, NH_2, OH, F). According to the standard geometrical model that is being used, three-coordinate nitrogen is taken to be planar trigonal if attached to an unsaturated atom as in aniline. Actually, an experimental microwave study by Lister and Tyler[25] shows that the NH_2 group is not planar. The HNH angle is found to be 113.9°, and there is a small inversion barrier. This is confirmed by an ultraviolet spectroscopic[26] study which gave a barrier height of 1.61 kcal mol^{-1}. To allow for this possibility in the theory, we have considered the C_s pyramidal form V



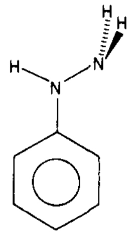
V

of aniline, in which the three bond angles at nitrogen are kept equal but permitted to be less than 120°. Optimization of the angle α leads to a theoretical value of 47.7° (nitrogen bond angle of 112.1°) and a barrier of 2.7 kcal mol^{-1}. This is somewhat too high. However, it should be noted that the same basis set gives too large a barrier for NH_3.[27]

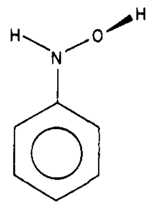
For the N-substituted anilines, we have used the planar standard model for nitrogen in most cases. *N*-Methylaniline is predicted to have the structure VI, which decreases steric interaction with an ortho hydrogen. Phenylhydrazine (VII) and *N*-phenylhydroxylamine (VIII) are both predicted to have



VI



VII



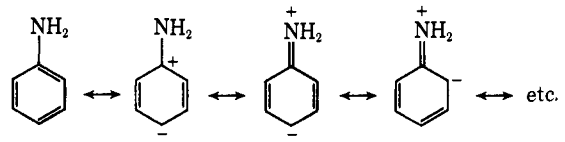
VIII

structures which keep lone pairs of electrons in orthogonal arrangements. *N*-Fluoroaniline was examined both in the N-planar arrangement and in a form corresponding to V with a tetrahedral nitrogen. This showed the nonplanar form to be substantially more stable (by 7.1 kcal mol^{-1}). It appears, therefore, that fluorine substitution increases the nonplanarity at nitrogen. The crystal structure of phenylhydrazine[28] also shows that the bonds at nitrogen are nonplanar, but neither this molecule nor *N*-phenylhydroxylamine has been investigated in detail here.

The stabilization energies listed in Table III show features similar to those of the substituted toluenes, further substitution on nitrogen leading to reduction of the stabilization effect. Allowance for nonplanar nitrogen in aniline improves the agreement with experiment, and it is probable that stabilization energies for the other compounds would be similarly modified. The value for C_6H_5NHF with tetrahedral nitrogen is +5.4 kcal mol^{-1}, indicating positive stabilization for all the substituents.

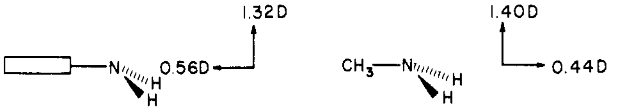
The charge densities in the anilines (Table III) show substantial π-charge donation from the nitrogen into the ring combined with σ withdrawal. The magnitude of the π donation is larger for the planar nitrogen arrangement, presumably because of the better overlap of the lone pair with the benzene π orbitals.

The π-charge distributions (Chart I), with large negative charges at the ortho and para positions, agree with those expected on the basis of contributions from the usual valence structures (including polarization structures) for aniline.



The π_{Ph-X} overlap populations (Table III) indicate considerable double-bond character in the C–N bond.

The calculated dipole moments of aniline (with optimized nitrogen bond angle) and methylamine (standard geometry) provide an interesting comparison.



The major difference is a *reversal* of the dipole moment component along the C–N axis, indicating a mesomeric component of approximately 1.0 D. This is very close to the experimental value of 1.02 D.[23] The inclination of the calculated moment is 67° to the aromatic plane, compared with experimental estimates [29,30] of 43°.

Phenol and Related Molecules. Phenol and the O-substituted derivatives C_6H_5OZ (Z = CH_3, NH_2, OH, F) were examined in a similar manner. Phenol itself is predicted to be planar, presumably because of the conjugation of the oxygen lone pair with the aromatic π electrons. The theoretical barrier is 5.2 kcal mol^{-1}, which is rather larger than experimental values of 3.28 and 3.36 (microwave)[31,32] and 3.47 (infrared)[33] kcal mol^{-1}. The high barrier in phenol may be associated with the moderately large degree of double-bond character in the C–O bond.

Anisole is predicted to be most stable in the orthogonal form if the standard model is used. However,

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York, N. Y., 1955). However, in the absence of such calculated data, we make comparisons with Me-X, and this should be adequate for our purposes here.

(24) Experimental dipole moments quoted in this paper are from ref 22.

(25) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

(26) J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectrosc.*, 20, 359 (1966).

(27) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 6377 (1971).

(28) S. Srinivasan and S. Swaminathan, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 127, 442 (1968).

(29) M. J. Aroney, R. J. W. LeFevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.*, *B*, 507 (1968).

(30) R. J. B. Marsden and L. E. Sutton, *ibid.*, 599 (1936).

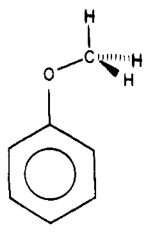
(31) H. Forest and B. P. Dailey, *J. Chem. Phys.*, **45**, 1736 (1966).

(32) T. Pedersen, N. W. Larsen, and L. Nygaard, *J. Mol. Struct.*, **4**, 59 (1969).

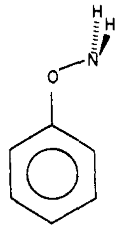
(33) H. D. Bist and D. R. Williams, *Bull. Amer. Phys. Soc.*, **11**, 826 (1966).

this result is influenced by the steric interaction with an ortho hydrogen in the cis (planar skeleton) form. If we allow for this by optimizing the COC bond angle for both forms, the energies of the two forms become very close, the cis form IX being slightly more stable. With this relaxation, it appears that the steric distortion in the planar skeleton form largely cancels the effect of extra conjugation with the lone-pair electrons. However, since the method used to allow for steric effects (variation of only one bond angle) is rather inflexible, it is probable that a fuller geometrical study would further lower the energy of IX. Alternatively, relief of steric interactions could be achieved by a small rotation about the C–O bond, with less distortion of the COC bond angle. Experimentally, the structure of anisole is somewhat uncertain. Crystallographic studies of some methoxybenzenes give planar skeleton structures,[34,35] and this is supported by a vibrational spectroscopic study of the liquid,[36] which gives a large barrier of about 6 kcal mol^{-1}. On the other hand, Kerr effect measurements in solution[37] indicate a nonplanar skeleton with a CCOC dihedral angle of about 20°.

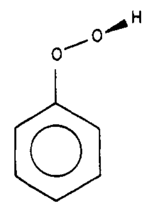
O-Phenylhydroxylamine is predicted to have the structure X, which is comparable to the lowest energy form of hydroxylamine itself. For phenyl hydroperoxide, we have only examined the orthogonal structure XI.



IX



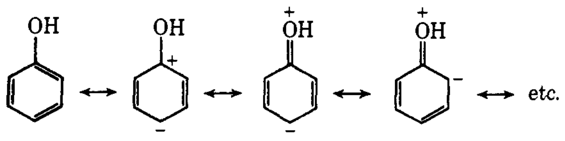
X



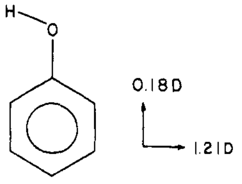
XI

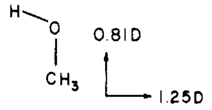
The stabilization energies listed in Table III again show decreased values with substitution for O-substituted phenols. The rather low value for anisole probably arises because of the considerable steric distortion in the cis form. However, the experimental number is comparable to that for phenol and does not seem to support the notion of steric destabilization. This again may be because our treatment of the steric effect has not used sufficient degrees of freedom to allow for relief in an adequate manner.

The charge densities for phenol again show considerable π donation from the oxygen p-type lone pair into the ring combined with σ withdrawal. Strong alternation of π charge in the ring is again evident, supporting the usual ideas on contributing valence structures.



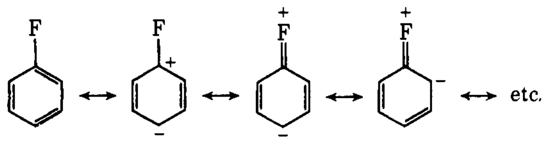
The calculated dipole moment of phenol (1.22 D) is lower than that of methanol (1.49 D), in agreement with experimental results (1.45 D *vs.* 1.70 D). The dipole moment components show that this is primarily





due to a decrease in the dipole component along the C–O axis in phenol, suggesting a mesomeric component of about 0.6 D. This agrees with the experimental value (0.6 D).[23] It is of interest to note that these effects still persist in the orthogonal form of these molecules. Thus, the orthogonal form of phenol still shows alternation of charge within the ring, with negative charges at the ortho and para positions. The π charge donation (0.049) is moderately large. Evidently, conjugation with the aromatic system is not eliminated but only reduced by rotation of the hydroxyl group.

Fluorobenzene. The stabilization energy in fluorobenzene is quite large, though somewhat smaller than in phenol. In C_6H_5F, the fluorine substituent interacts with the benzene ring by withdrawing σ electrons and donating π electrons. The charge distribution is similar to that found previously with optimized exponents[7] and suggests the valence structures



The mesomeric contribution to the dipole moment opposes the C–F bond moment. Accordingly, the calculated dipole moment of fluorobenzene (0.93 D) is smaller than that of methyl fluoride (1.13 D), which agrees with the experimental result (dipole moments of 1.60 and 1.85 D, respectively).

Styrene. The C═C bond in styrene can conjugate most effectively with the ring in the planar (CCCC cis) conformation, and this is found to be the most stable form. The standard model gives a rather small barrier of 1.90 kcal mol^{-1}. However, the planar form involves steric repulsions between hydrogens, so further calculations were carried out in which the C—C═C angle was optimized (the corresponding CH bond being kept on the bisector of this angle). The CCC angle opened in both conformations, the larger change occurring in the planar form (to 128.0°). The barrier is increased to 4.42 kcal mol^{-1}.

There is little variation in π charge in styrene, either within the ring or in the double bond, most atoms having π-electron populations close to 1.000. The resultant dipole moment is close to zero and smaller than in propene, in agreement with experiment.

Benzaldimine. This molecule can have the two planar isomeric forms syn (XII) or anti (XIII). The syn form is found to be more stable, presumably because of steric interaction in XIII. There appears to be no experimental information.

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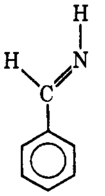
(34) T. H. Goodwin, M. Przykylaska, and J. M. Robertson, *Acta Crystallogr.*, 3, 279 (1950).

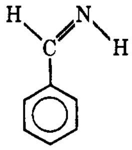
(35) G. W. R. Bartindale, M. M. Crowder, and K. A. Morley, *ibid.*, 12, 111(1959).

(36) N. L. Owen and R. E. Hester, *Spectrochim. Acta, Part A*, 25, 343 (1969).

(37) M. J. Aroney, R. J. W. Le Fevre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc. B*, 666 (1969).



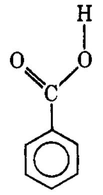
XII



XIII

Benzaldehyde and Related Molecules. We have considered the set of molecules C_6H_5COZ with Z = H, CH_3, NH_2, OH, and F. The twofold rotational barriers were examined for benzaldehyde, acetophenone, and benzoic acid. For benzaldehyde, the theory gives 6.6 kcal mol^{-1}, somewhat larger than the microwave[38] and infrared[39] values of 4.90 and 4.66 kcal mol^{-1}, respectively. For acetophenone, the theoretical barrier (4.4 kcal mol^{-1}) is somewhat smaller than in benzaldehyde, in agreement with experiment (3.1 kcal mol^{-1}).[40] However, this may partly be due to steric repulsion between the methyl group and the ortho hydrogen, for which no allowance was made.

The most stable form of benzoic acid is found to be planar (as in the crystal structure[41]), with CCOH trans (XIV). The same conformation of the carboxyl group was found in the corresponding theoretical treatment of formic acid[6] and also in the crystal structure[42] of *p*-aminobenzoic acid. The calculated barrier in benzoic acid (5.76 kcal mol^{-1}) is slightly smaller than in benzaldehyde, consistent with the reduced double-bond character in the Ph–C bond (as indicated by $\pi_{\text{Ph-X}}$). A probable reason is that the strong interaction between the C=O bond and the 2p orbital on the hydroxyl oxygen reduces the interaction between the C=O bond and the aromatic ring.

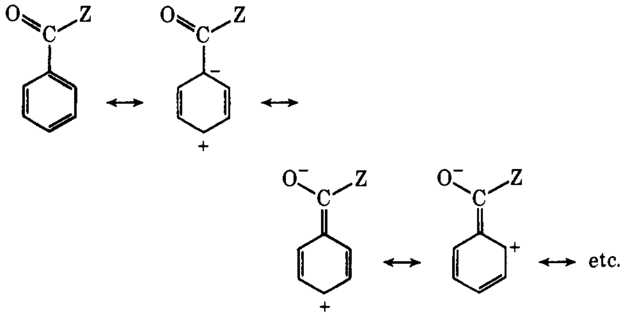


XIV

In benzamide, there is a further reduction in $\pi_{\text{C-C}}$ in the planar form and, in addition, there is unfavorable steric interaction for this structure. Additional calculations on conformations obtained by 30 and 90° rotations from the cis form give the lowest energy for CCCO = 30°, suggesting that benzamide is nonplanar. However, no attempt was made to optimize any bond angles. The experimental crystal structure[43] shows an angle of twist of 26° about the C–C bond.

The theoretical stabilization energies for this group of substituents (Table III) are all positive, the small values for acetophenone and benzamide probably being due to inadequate treatment of steric repulsion. The relatively low stabilization energies for benzamide and benzoic acid reflect reduced interaction between the C=O bond and the aromatic ring owing to the competing interaction between lone-pair electrons on NH_2 or OH and the C=O bond, as mentioned above. An interesting point is that the stabilization energies for the orthogonal forms of the benzaldehydes are all small and negative.

The charge distributions all show withdrawal of π electrons from the ring, the resulting positive charge being mainly associated with the ortho and para positions. This is in agreement with the predictions of resonance theory in terms of structures



The ortho and para net π charges, however, are quite small (about +0.02). The mesomeric moment reinforces the normal carbonyl group moment, hence the calculated resultant moment for benzaldehyde (1.90 D), for example, is larger than for acetaldehyde (1.75 D), in agreement with experiment (2.98 *vs.* 2.69 D). The moment in the orthogonal form of benzaldehyde (1.78 D), on the other hand, is close to the acetaldehyde value as expected.

N-**Phenylformaldimine.** Only a single computation was carried out on this molecule for a planar structure using the standard model. This gives a rather unstable form, reflected in a negative stabilization energy (Table III). However, this is probably due to the failure to take account of steric repulsion between a β hydrogen and an ortho hydrogen (particularly since the standard model uses a tetrahedral bond angle for nitrogen).

Phenyldiimide. Both cis and trans isomers of this molecule were examined in planar configurations using the standard geometrical model. The cis form again involves steric interaction with an ortho hydrogen, and we have not attempted to allow for this effect. This limitation does not apply to the trans isomer. Here the theoretical stabilization energy is positive, but quite small (1.7 kcal mol^{-1}), indicating only a weak interaction.

Nitrosobenzene and Nitrobenzene. These molecules were examined in planar and orthogonal forms. Both molecules are found to be planar, in agreement with experimental findings.[44,45] For nitrosobenzene, theoretical and experimental[46] twofold barriers are 4.8 and 3.9 kcal mol^{-1}. For nitrobenzene, corresponding numbers are 5.8 and *ca.* 2.9 (±1.4)[47] kcal mol^{-1}. The stabilization energies are both small positive and become negative in the orthogonal conformations.

Both substituents withdraw π electrons from the ring, particularly from the ortho and para positions, this effect being most pronounced for nitrobenzene.

(38) R. K. Kakar, E A. Rinehart, C. R. Quade, and T. Kojima, *J. Chem. Phys.*, **52**, 3803 (1970).

(39) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

(40) F. A. Miller, W. G. Fateley, and R. E. Witkowski, *ibid., Part A*, **23**, 891 (1967).

(41) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Crystallogr.*, **8**, 157 (1955).

(42) T. F. Lai and R. E. Marsh, *ibid*, **22**, 885 (1967).

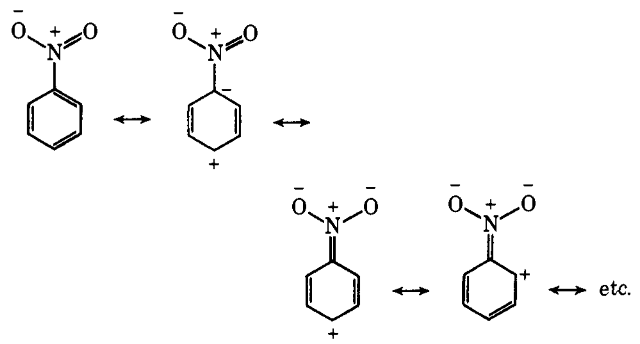
(43) B. R. Penfold and J. C. B. White, *ibid.*, **12**, 130 (1959).

(44) Y. Hanyu and J. E. Boggs, *J. Chem. Phys.*, **43**, 3454 (1965).

(45) J. Trotter, *Acta Crystallogr.*, **12**, 884 (1959).

(46) Y. Hanyu, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **45**, 4725 (1966).

(47) H. J. Hog, L. Nygaard, and G. O. Sorensen, *J. Mol. Struct.*, **7**, 111 (1970).



The calculated dipole moment for planar nitrobenzene (4.26 D) is large, considerably larger than for nitromethane (3.33 D), in good agreement with experiment (4.22 *vs.* 3.46 D). The mesomeric component is thus about 0.9 D. In the orthogonal form of nitrobenzene, the theoretical moment is lowered to 3.99 D. An interesting comparative value is the experimental dipole moment for nitromesitylene (3.7 D), in which the nitro group is believed to be approximately orthogonal to the aromatic plane.

The π-electron distributions in the orthogonal forms of nitrosobenzene and nitrobenzene show some interesting features. Whereas the substituent withdraws π electrons from the ring in planar nitrosobenzene, there is π-charge donation from the nitrogen lone pair in the orthogonal form, and the charge alternation is reversed (see Chart I). This may have interesting consequences in the properties of nitrosobenzenes constrained to be orthogonal. In the orthogonal form of nitrobenzene, this effect is not observed.

Phenylacetylene, Benzonitrile, and Phenyl Isocyanide. Apart from the fact that these three triply bonded molecules all have moderately large stabilization energies, the main features of interest are the charge distributions.

In phenylacetylene, both π and σ electrons are withdrawn from the ring. There is alternation of π charge in the ring with small positive charges at the ortho and para positions. The calculated dipole moment (0.52 D) is moderately close to the experimental value (0.73 D). The dipole direction Ph^+–CCH^- confirms that deduced from the experimental moments of substituted phenylacetylenes.[22]

In benzonitrile, there is larger π- and σ-electron withdrawal from the ring and larger positive charges are found at the ortho and para positions. The mesomeric component reinforces the ordinary C–CN moment, leading to a theoretical dipole moment for benzonitrile (3.65 D) larger than in acetonitrile (3.06 D), in agreement with experiment (4.18 *vs.* 3.92 D).

Finally, in phenyl isocyanide, there is still larger σ-electron withdrawal from the ring, but in this case there is π-electron donation. The mesomeric component thus opposes the C–NC moment, and this may lead to a moment in phenyl isocyanide smaller than in methyl isocyanide. This is, in fact, observed experimentally (3.56 *vs.* 3.85 D), but the theoretical moments are fairly close together (3.17 and 3.08 D, respectively).

Conclusions

Several important points emerge from this application of *ab initio* molecular orbital theory.

(1) Conformations of substituted benzenes are determined largely by conjugation effects. When the conformations most favored by conjugation involve steric interactions, bond angle or torsional distortions occur.

(2) Stabilization energies for the lowest energy forms of these molecules are always positive[48] (*i.e.*, the phenyl group is stabilizing compared with methyl). However, when the phenyl group is perpendicular to the π system of the substituent as, for example, in the orthogonal forms of nitrobenzene and benzaldehyde, it is sometimes destabilizing. This predicted behavior should be reflected in the properties of derivatives of these molecules constrained to be in the orthogonal conformation.

(3) Absolute values of calculated electric dipole moments are generally too low, but most experimental trends are reproduced. In particular, calculated and experimental mesomeric moments are in close agreement. The theoretical charge distributions support many of the ideas of classical organic chemistry. However, in addition to the *transfer* of π electrons from the substituent into the aromatic ring (implied by the commonly drawn contributing valence structures), *polarization* of the π electrons within the ring is also important. Charge distributions in orthogonal conformations (*e.g.*, in nitrosobenzene) can be strikingly different from those in planar forms.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. GP-25617.

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[48] See also footnote *g* to Table III.