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Conformations, Stabilities, and Charge Distributions in 2- and 3-Monosubstituted Furans. An ab Initio Molecular Orbital Study

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Abstract: Ab initio molecular orbital theory with the minimal STO-3G basis set is used to obtain a theoretical structure for furan and to study the conformations, stabilities, and charge distributions of 50 2- and 3-substituted furans. The conformational preferences can be rationalized in terms of conjugative, hyperconjugative, dipolar, and steric effects. The fact that the carbon-carbon bonds in furan can be distinguished as having more (C2-C3) or less (C3-C4) double bond character manifests itself in conformational preferences—a single bond of the substituent eclipsing C2-C3—which do not exist in substituted benzenes. The stabilizing effect of substituents attached to furan and benzene rings is compared. Because the furyl group prefers to act as a π -electron donor and a σ -electron acceptor, furan is stabilized relative to benzene by substituents which are π -electron acceptors and σ -electron donors, and destabilized by substituents which are π -electron donors and σ -electron acceptors. These effects are generally more pronounced at the 2 than at the 3 position.

Introduction

The furan nucleus forms an important subunit in many interesting organic molecules and the physical and chemical properties of furans have consequently received considerable attention in the literature.¹ Of particular interest is the effect of substituents in the furan ring. Various experimental approaches have been adopted in order to rationalize and classify such effects. For example, reaction rates^{2,3} and infrared^{4,5} and nuclear magnetic resonance⁶ spectral properties of substituted furans have been correlated with Hammett and related substituent constants. On the other hand, most of the previous theoretical studies, which include both π -electron⁷⁻¹² and all valence electron¹³⁻¹⁸ semiempirical approaches, have been primarily concerned with furan itself and in particular with its electron distribution. Little theoretical attention has been given to the conformational and energetic properties of substituted furans. Several ab initio calculations on furan have been carried out¹⁹⁻²³ but the only ab initio studies on substituted furans which have been reported to date are conformational investigations of furan-2- and -3-carbaldehyde.²³

In this paper, we report the results of a systematic study, using ab initio molecular orbital theory, of furan and a number of 2- and 3-substituted furans. Several aspects of the subject are considered in detail. Firstly, we obtain a complete theoretical structure for furan itself. Secondly, we determine, for the substituted furans, the preferred conformations and the rotational barriers separating the rotational isomers. Thirdly, we examine the effect of the substituents on the stability of the furan ring. And finally, we consider the charge distributions and dipole moments in all systems. Extensive comparison is

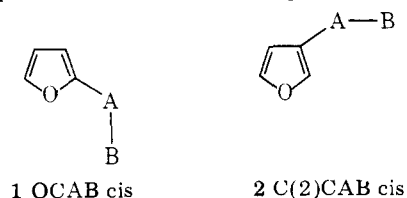
made with substituted benzenes for which corresponding results are already available.²⁴

Method and Results

Standard LCAO SCF molecular orbital theory was used. All calculations were performed using a modified version of the Gaussian 70 system of programs²⁵ with the minimal STO-3G basis set.²⁶

For furan, a full optimization of all bond lengths and bond angles was carried out using a gradient optimization procedure,²⁷ subject only to a C_{2v} symmetry constraint. The optimized structure is shown in Figure 1.

For the substituted furans, the geometry of the furan nucleus was taken from the above STO-3G optimized structure (Figure 1) while standard²⁸ bond lengths and angles were used for the substituent groups. Cis, orthogonal, and trans conformations were generally considered, these having values of the dihedral angle θ of 0, 90, and 180°, respectively, where $\theta = 0^\circ$ is defined as shown in **1** and **2** for the 2- and 3-substituted furans. Conformations with θ having intermediate values were not examined, although it is recognized that, in some cases, these may represent stationary points (i.e., maxima or minima) in the rotational potential surface. For example, for an asymmetric



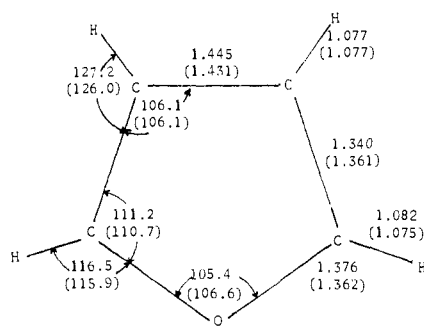
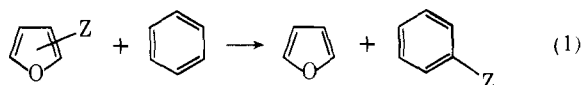


Figure 1. Comparison of STO-3G and microwave (in parentheses) structural parameters.

substituent with planar cis ($\theta = 0^\circ$) and trans ($\theta = 180^\circ$) isomers of unequal energy, simple symmetry arguments predict that the maximum in the potential curve for internal rotation should not occur at $\theta = 90^\circ$. In practice, the deviation from $\theta = 90^\circ$ may be quite small. Thus, in an STO-3G study of heteroaromatic aldehydes derived from furan, pyrrole, and pyridine, we found^{23a} a maximum deviation of 4° . In this paper, we simply compare the energies of exactly planar ($\theta = 0, 180^\circ$) and exactly orthogonal ($\theta = 90^\circ$) structures. Within the substituents, a staggered arrangement was used for bonds connecting two atoms with tetrahedral bond angles unless otherwise specified. In some molecules, use of the standard geometry gave rise to unrealistic steric repulsions. Geometry optimization of critical bond angles was therefore carried out in these cases, the resulting flexible rotor model having been shown in previous situations^{24,29} to give a reasonable description of certain molecular properties. Calculated total and relative energies for conformations of 2- and 3-substituted furans are summarized in Table I.

Our energetic data were analyzed in terms of substituent stabilization energies. A measure of the stabilizing effect of a substituent Z on the furan ring (compared with its effect in benzene) is provided by energy changes (ΔE_{SE}) in formal reactions of the type shown in (1). For this reaction there is re-



tention of the number of bonds of a given formal type and previous work³⁰⁻³² has suggested that such so-called *isodesmic* reactions are reasonably well described by relatively simple levels of molecular orbital theory due to a cancellation of the errors associated with electron correlation and the deficiencies of a limited basis set. Theoretical stabilization energies (ΔE_{SE}) calculated utilizing previously reported data for benzene and substituted benzenes are shown in Table II. A positive value for ΔE_{SE} implies that the substituent has a stabilizing effect in furan relative to its effect in benzene.

Finally, directly calculated dipole moments and charge distributions derived using the Mulliken approach³³ are reported. The dipole moments are included in Table II while total σ and π charges (q_σ and q_π , respectively) donated to the ring by the substituent are compared with the values obtained for the corresponding substituted benzenes, q_σ (B) and q_π (B), in Table III. Note that a negative value of q corresponds to donation of negative charge, i.e., electron donation; conversely, a positive value of q corresponds to electron withdrawal by the substituent. Calculated π -electron distributions are presented in Figures 2 and 3.

Discussion

Furan. Our fully optimized structure for furan is compared with the microwave structure³⁴ in Figure 1. Agreement between the two structures is good with the largest deviations

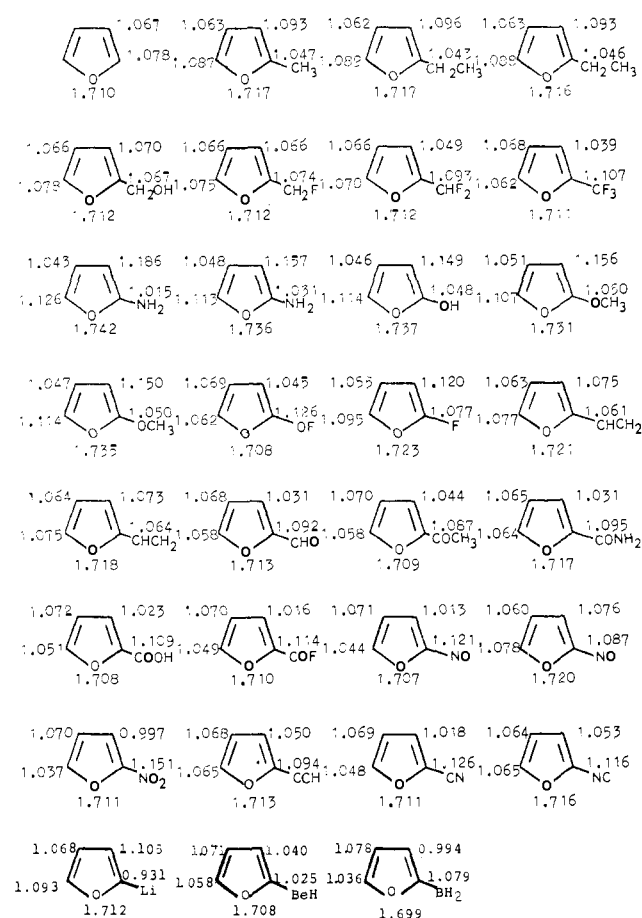
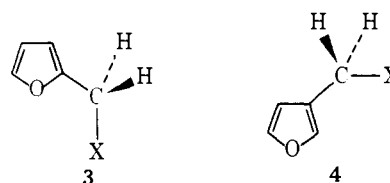


Figure 2. π -Electron populations in 2-substituted furans.

being 0.021 \AA in bond lengths and 1.2° in bond angles. The dipole moment is characteristically underestimated by the STO-3G basis set ($\mu = 1.77 \times 10^{-30} \text{ C m}$; cf. 2.21 ± 0.02 from the microwave data³⁵).

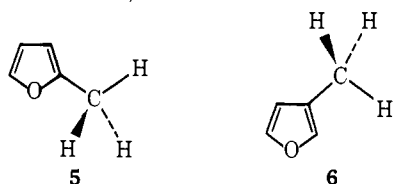
Previous ab initio calculations for furan¹⁹⁻²² have been based on the microwave structure. Both Palmer et al.²¹ and Siegbahn²² have employed large basis sets which include polarization functions. The STO-3G π -electron distribution predicts a greater π -electron density at the 2 position than at the 3 position but we note that this result is basis set dependent.²² In addition, we find a higher coefficient at C(2) than at C(3) in the highest occupied molecular orbital (HOMO) and this manifests itself in enhanced conjugative interaction with π -electron accepting substituents in the 2-substituted derivatives described below.

2- and 3-Methylfurans and Related Molecules: FuCH₂X, X = H, CH₃, OH, and F. The first group of substituted furans which we discuss is the set of 2- and 3-substituted derivatives FuCH₂X with X = H, CH₃, OH, and F. Calculations were performed on conformations generated by internal rotation (θ) about the Fu-CH₂X bond. Conformations with $\theta = 0^\circ$ are



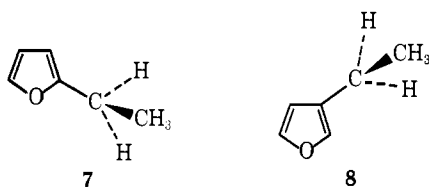
For both 2- and 3-methylfuran, microwave structures^{36,37} are available and provide interesting comparisons with the results of the calculations presented here. In striking contrast to toluene, for which there is almost free internal rotation for

the methyl group, the monomethylfurans exhibit distinct conformational preferences. This difference in behavior may be attributed to the existence of some degree of bond fixation in furan, i.e., the bonds may be qualitatively distinguished as having more double (C2-C3) or more single (C2-O and C3-C4) bond character, whereas in benzene the bonds are indistinguishable. Thus for 2-methylfuran, the trans conformation (**5**) is preferred, this structure incorporating the favorable disposition of the methyl group^{38,39} in which the double bond of the furan ring is eclipsed and the single bond staggered. The calculated rotational barrier in 2-methylfuran is 2.5 kJ mol⁻¹, somewhat less than the experimental value³⁶ of 5.0 kJ mol⁻¹. To some extent, the difference may be due to a lack of flexibility in the rotating methyl group which would be expected to favor slightly the cis form. For 3-methylfuran, the favorable methyl group configuration, i.e., methyl C-H eclipsing the double bond, occurs in the cis conformation (**6**),



which is indeed predicted to be the most stable, in agreement with experiment.³⁷ The calculated barrier to rotation (3.1 kJ mol⁻¹) is again a little lower than the microwave value (4.6 kJ mol⁻¹).³⁷

For 2- and 3-ethylfuran, a staggered arrangement about the ethyl C-C bond was assumed. Using standard bond angles, orthogonal ($\theta = 90^\circ$, **7**, **8**) structures are found to be more



stable than planar structures ($\theta = 0, 180^\circ$) for both molecules as for ethylbenzene.²⁴

In view of the likely steric interaction in the planar structures, however, further calculations were undertaken for 2-ethylfuran in which the ethyl CCC angle was optimized, the CCH angles being constrained to maintain a tetrahedral arrangement. The CCC angle is found to widen for each of the cis, trans, and orthogonal forms, but predictably the effect is slightly less for the last of these conformations. The orthogonal structure (**7**) remains the lowest energy form, with the cis and trans structures lying higher in energy by 3.9 and 0.8 kJ mol⁻¹, respectively. Results with the standard geometry for 3-ethylfuran predict the cis and trans forms to lie 3.5 and 7.6 kJ mol⁻¹, respectively, above the orthogonal structure (**8**). The distinct energy difference between the planar conformations of both molecules is somewhat surprising since a comparison of non-bonded interatomic distances within the two molecules reveals no significant difference in steric interactions between the cis and trans forms of each. Apparently the tendency of single bonds to be staggered with respect to other single bonds and to eclipse double bonds is an important influence in determining the relative energies of the molecules discussed in this section. In this respect, the situation is related to that for 1-butene.⁴⁰ The greater energy differences between planar and orthogonal forms in 3-ethylfuran compared to those for 2-ethylfuran are consistent with the previously recorded results for ethylbenzene²⁴ and the 1-propyl cation.⁴¹ The greater the positive charge in the p orbital at the sp² center, the greater the expected hyperconjugative interaction of the C-C bond and consequently the more stabilized the orthogonal form. Undoubtedly, steric effects also play an important role in deter-

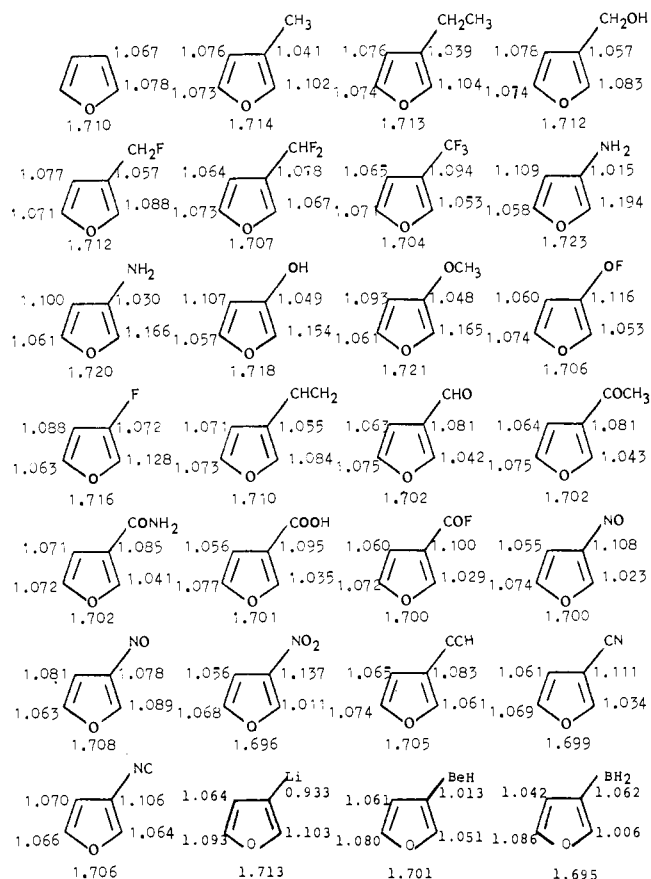
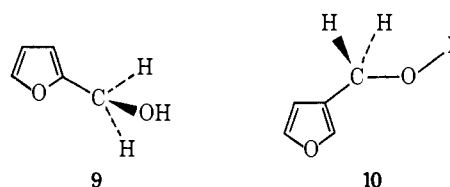


Figure 3. π -Electron populations in 3-substituted furans.

mining the preference for orthogonal over planar conformations. We have not considered intermediate structures (e.g., $0^\circ < \theta < 90^\circ$) for the ethylfurans. Furfuryl alcohol is also found to adopt an orthogonal arrangement (**9**) in preference to a planar trans form, although the energy difference (1.3 kJ mol⁻¹) is not very great. In this, it differs from benzyl alcohol and 3-furylmethyl alcohol, where planar conformations are favored. This difference may be attributed to hyperconjugative electron withdrawal by the C-OH bond in **9** which is desirable because of the enhanced electron density at the 2 position of furan. The cis conformation of furfuryl alcohol is of high energy, being disfavored both by the disposition of the substituent with respect to the furan double and single bonds and by the proximity of two parallel component dipole moments. The cis conformation (**10**) of 3-furylmethyl alcohol, on the other hand, maintains the favorable configuration of the substituent and represents the lowest energy molecular conformation, being



slightly favored over the orthogonal form. Our result for the favored conformation of furfuryl alcohol is at variance with a semiempirical study⁴² where a planar structure was predicted.

3-Fluoromethyl- and 3-difluoromethylfuran behave analogously to the corresponding substituted benzenes²⁴ with the cis-fluorine (**11**) and cis-hydrogen (**12**) conformations being preferred, respectively, although in the former case the orthogonal structure effectively has the same energy. For 2-fluoromethylfuran, an orthogonal conformation (**13**) is

Table I. Calculated Total Energies (hartrees) and Relative Energies (kJ mol⁻¹) for 2- and 3-Monosubstituted Furans

Substituent (-Z)	2-Substituted furan			3-Substituted furan		
	Conformation	Total energy	Rel energy	Conformation	Total energy	Rel energy
-H		-225.751 26			-225.751 26	
-CH ₃	OCCH cis	-264.339 27	2.47	C(2)CCH cis	-264.336 77	0
	OCCH orthogonal	-264.339 73	1.25	C(2)CCH orthogonal	-264.336 17	1.56
	OCCH trans	-264.340 21	0	C(2)CCH trans	-264.335 59	3.11
-CH ₂ CH ₃ ^a	OCCC cis	-302.917 22	5.02	C(2)CCC cis	-302.914 23	3.49
	OCCC orthogonal	-302.919 13	0	C(2)CCC orthogonal	-302.915 55	0
	OCCC trans	-302.918 53	1.59	C(2)CCC trans	-302.912 67	7.57
-CH ₂ CH ₃ ^a	OCCC cis; C(2)CC = 112.7 °	-302.918 15	3.94			
	OCCC orthogonal; C(2)CC = 112.0°	-302.919 65	0			
	OCCC trans; C(2)CC = 112.5°	-302.919 33	0.82			
-CH ₂ OH ^b	OCCHO cis	-338.157 09	9.21	C(2)CCO cis	-338.158 66	0
	OCCHO orthogonal	-338.160 60	0	C(2)CCO orthogonal	-338.158 22	1.17
	OCCHO trans	-338.160 09	1.33	C(2)CCO trans	-338.157 24	3.72
-CH ₂ F	OCCF cis	-361.779 98	7.89	C(2)CCF cis	-316.780 88	0
	OCCF orthogonal	-361.782 98	0	C(2)CCF orthogonal	-361.780 83	0.14
	OCCF trans	-361.782 27	1.87	C(2)CCF trans	-361.779 67	3.18
-CHF ₂	OCCH cis	-459.242 38	0	C(2)CCH cis	-459.242 28	0
	OCCH orthogonal	-459.240 39	5.22	C(2)CCH orthogonal	-459.241 18	2.89
	OCCH trans	-459.241 84	1.40	C(2)CCH trans	-459.241 61	1.76
-CF ₃	OCCF cis	-556.713 82	2.16	C(2)CCF cis	-556.716 37	0
	OCCF orthogonal	-556.714 24	1.06	C(2)CCF orthogonal	-556.716 05	0.84
	OCCF trans	-556.714 64	0	C(2)CCF trans	-556.715 70	1.76
-NH ₂	NH ₂ planar	-280.065 68		NH ₂ planar	-280.059 35	
	Pyramidal N	-280.071 60		Pyramidal N	-280.065 71	
-OH	OCOH cis	-299.592 42	0	C(2)COH cis	-299.583 92	0.57
	OCOH orthogonal	-299.588 40	10.57	C(2)COH orthogonal	-299.580 10	10.61
	OCOH trans	-299.590 21	5.80	C(2)COH trans	-299.584 14	0
-OCH ₃ ^a	OCOC cis	-338.171 14	1.21	C(2)COC cis	-338.164 19	0
	OCOC orthogonal	-338.171 19	1.07	C(2)COC orthogonal	-338.163 44	1.97
	OCOC trans	-338.171 60	0	C(2)COC trans	-338.162 29	4.98
-OCH ₃ ^a	OCOC cis; C(2)OC = 113.7	-338.172 60	0			
	OCOC orthogonal; C(2)OC = 111.6	-338.171 43	3.06			
	OCOC trans; C(2)OC = 112.5	-338.172 25	0.92			
-OF	OCOF cis	-396.987 30	11.30	C(2)COF cis	-396.985 01	2.00
	OCOF orthogonal	-396.991 61	0	C(2)COF orthogonal	-396.985 77	0
	OCOF trans	-396.986 71	12.86	C(2)COF trans	-396.984 83	2.47
-F		-323.211 81			-323.205 33	
-CHCH ₂	OCCC cis	-301.697 08	0	C(2)CCC cis	-301.691 52	2.03
	OCCC orthogonal	-301.687 62	24.83	C(2)CCC orthogonal	-301.685 50	17.84
	OCCC trans	-301.695 92	3.04	C(2)CCC trans	-301.692 30	0
-CHCH ₂	OCCC cis; C(2)CC = 124.4	-301.698 05	0			
	OCCC orthogonal; C(2)CC = 123.7	-301.688 24	25.75			
	OCCC trans; C(2)CC = 124.9	-301.697 19	2.24			
-CHO	OCCHO cis	-336.976 95	4.13	C(2)CCO cis	-336.977 23	0
	OCCHO orthogonal	-336.967 53	28.88	C(2)CCO orthogonal	-336.968 12	23.93
	OCCHO trans	-336.978 53	0	C(2)CCO trans	-336.977 23	0.01
-COCH ₃ ^c	OCCHO cis	-375.566 44	4.99	C(2)CCO cis	-375.566 32	0
	OCCHO orthogonal	-375.558 02	27.09	C(2)CCO orthogonal	-375.558 46	20.64
	OCCHO trans	-375.568 34	0	C(2)CCO trans	-375.566 24	0.20
-CONH ₂ ^d	OCCHO cis	-391.295 84	11.12	C(2)CCO cis	-391.296 65	0
	OCCHO orthogonal	-391.289 67	27.33	C(2)CCO orthogonal	-391.290 66	15.70
	OCCHO trans	-391.300 08	0	C(2)CCO trans	-391.295 89	2.00
-COOH ^e	OCC=O cis	-410.833 31	1.04	C(2)CC=O cis	-410.835 14	0.22
	OCC=O orthogonal	-410.825 45	21.67	C(2)CC=O orthogonal	-410.827 18	21.12
	OCC=O trans	-410.833 71	0	C(2)CC=O trans	-410.835 22	0
-COF	OCFO cis	-434.449 82	2.47	C(2)CCO cis	-434.451 96	0
	OCFO orthogonal	-434.441 87	23.32	C(2)CCO orthogonal	-434.443 91	21.14
	OCFO trans	-434.450 75	0	C(2)CCO trans	-434.451 82	0.38
-NO	OCNO cis	-352.680 09	0.76	C(2)CNO cis	-352.677 46	3.70
	OCNO orthogonal	-352.666 65	36.07	C(2)CNO orthogonal	-352.667 82	29.01
	OCNO trans	-352.680 38	0	C(2)CNO trans	-352.678 87	0

Table I (Continued)

Substituent (-Z)	2-Substituted furan			3-Substituted furan		
	Conformation	Total energy	Rel energy	Conformation	Total energy	Rel energy
-NO ₂	NO ₂ planar	-426.437 39	0	NO ₂ planar	-426.440 59	0
	NO ₂ orthogonal	-426.429 04	21.94	NO ₂ orthogonal	-426.432 49	21.26
-CCH		-300.482 24			-300.481 96	
-CN		-316.302 71			-316.304 74	
-NC		-316.268 15			-316.267 09	
-Li		-232.478 73			-232.473 07	
-BeH		-240.193 00			-240.193 24	
-BH ₂		-250.711 81			-250.709 80	

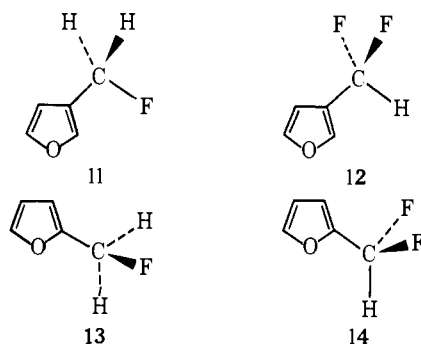
^a Methyl group staggered. ^b Methylene group staggers O-H bond. ^c Methyl C-H eclipses C=O. ^d Amino coplanar with C=O. ^e OCOH cis.

Table II. Dipole Moments (10⁻³⁰ C m)^a and Stabilization Energies Calculated for Reaction 1 (ΔE_{SE} , kJ mol⁻¹) for 2- and 3-Substituted Furans

Substituent (Z)	Dipole moment ^b		Total energy ^c PhZ, hartrees	Stabilization energy ^b	
	2-FuZ	3-FuZ		2-FuZ	3-FuZ
-H	1.77	1.77	-227.890 06		
-CH ₃	1.60	2.56	-266.473 82	13.6	4.6
-CH ₂ CH ₃	1.60	2.62	-305.053 33	12.1	2.7
-CH ₂ CH ₃ optimized	1.60		-305.053 87	12.0	
-CH ₂ OH	4.89	6.60	-340.296 28	8.2	3.1
-CH ₂ F	4.33	4.53	-363.918 85	7.7	2.2
-CHF ₂	4.39	3.03	-461.380 23	2.5	2.2
-CF ₃	6.13	3.87	-558.854 57	-5.1	1.6
-NH ₂ planar	3.95	5.24	-282.204 58	-0.3	-16.9
-NH ₂ pyramidal	5.10	5.59	-282.208 92	3.9	-11.6
-OH	3.40	6.25	-301.728 61	6.9	-14.9
-OCH ₃	5.89	2.38	-340.303 93	17.0	-2.5
-OCH ₃ optimized	3.35		-340.304 29	18.7	
-OF	6.67	4.41	-399.128 07	6.1	-9.2
-F	3.92	2.42	-325.349 39	3.2	-13.8
-CHCH ₂	1.35	1.49	-303.824 79	29.1	16.6
-CHCH ₂ optimized	1.49		-303.829 79	18.5	
-CHO	6.00	6.10	-339.115 40	5.1	1.7
-COCH ₃	8.32	6.62	-377.702 19	7.7	4.4
-CONH ₂	8.49	9.83	-393.430 94	20.8	11.8
-COOH	3.45	2.02	-412.973 47	-2.5	1.2
-COF	8.59	7.03	-436.590 36	-2.1	1.1
-NO	8.88	6.10	-354.815 88	8.7	4.7
-NO ₂	14.71	12.01	-428.583 23	-18.5	-10.1
-CCH	2.42	0.99	-302.619 70	3.5	2.8
-CN	12.31	10.15	-318.443 30	-4.7	0.6
-NC	10.51	8.75	-318.408 90	-5.1	-7.9
-Li	16.82	17.92	-234.600 99 ^d	43.4	28.6
-BeH	3.23	1.07	-242.323 85 ^d	20.9	21.5
-BH ₂	4.43	1.51	-252.842 14 ^d	22.2	17.0

^a 10⁻³⁰ C m = 0.2998 D. ^b Dipole moments and stabilization energies reported for the lowest energy conformations in Table I. ^c Total energy of the corresponding substituted benzene (from ref 24 unless otherwise noted) used to calculate ΔE_{SE} . ^d This work.

adopted, this again being favored by hyperconjugative electron withdrawal into the C-F bond. The cis form of 2-fluoromethylfuran is rather strongly disfavored, probably for similar



reasons to those noted above for cis furfuryl alcohol. 2-Difluoromethylfuran shows a preference for the planar cis structure (14) in which dipole-dipole interactions are minimized and steric crowding of the larger fluorine atoms is relieved. In addition 14 would be favored by C-F hyperconjugative interactions. For 2- and 3-trifluoromethylfuran, the favored conformations are analogous to those for the corresponding methylfurans, i.e., with C-F bonds eclipsing a C=C double bond of the furan ring.

In general, for the 3-substituted furans, the favored conformations are the same as for the corresponding benzene derivatives. The only orthogonal structure is obtained for 3-ethylfuran, and here the barriers to rotation to the planar forms are reduced from that for ethylbenzene demonstrating the decrease in steric interaction that is to be expected in going to a five-membered ring. For the 2-substituted furans, substitu-

Table III. Calculated Mulliken Charges and π -Overlap Populations for 2- and 3-Substituted Furans

Substituent (-Z)	Mulliken charges ^a						PhZ ^c	π_{R-Z} ^b	
	PhZ ^c		2-FuZ		3-FuZ			2-FuZ	3-FuZ
	q_σ (B)	q_π (B)	q_σ (2F)	q_π (2F)	q_σ (3F)	q_π (3F)			
-H	-0.063	0	-0.082	0	-0.072	0	0	0	0
-CH ₃	-0.007	-0.008	-0.035	-0.007	-0.019	-0.006	0.009	0.009	0.009
-CH ₂ CH ₃			-0.043	-0.007	-0.027	-0.005		0.011	0.010
-CH ₂ CH ₃ ^d	-0.013	-0.005	-0.042	-0.006			0.013	0.012	
-CH ₂ OH	+0.002	-0.007	-0.023	+0.007	0.000	-0.004	0.009	0.015	0.008
-CH ₂ F	+0.003	-0.006	-0.030	+0.006	-0.009	-0.004	0.008	0.015	0.008
-CHF ₂	+0.009	+0.010	-0.021	+0.011	-0.006	+0.011	0.018	0.018	0.018
-CF ₃	+0.021	+0.011	-0.010	+0.013	+0.007	+0.012	0.017	0.018	0.017
-NH ₂ ^e	+0.159	-0.120	+0.133	-0.112	+0.142	-0.100	0.063	0.051	0.046
-NH ₂ ^f	+0.140	-0.095	+0.109	-0.086	+0.120	-0.076	0.048	0.037	0.033
-OH	+0.185	-0.102	+0.153	-0.094	+0.162	-0.085	0.052	0.041	0.038
-OCH ₃			+0.150	-0.094	+0.164	-0.087		0.046	0.044
-OCH ₃ ^d	+0.192	-0.105	+0.154	-0.096			0.057	0.045	
-OF	+0.226	-0.090	+0.146	-0.010	+0.161	-0.008	0.044	0.033	0.031
-F	+0.215	-0.080	+0.183	-0.071	+0.192	-0.067	0.038	0.030	0.030
-CHCH ₂			-0.029	+0.003	-0.013	+0.008		0.052	0.050
-CHCH ₂ ^d	+0.003	+0.006	-0.028	+0.006			0.053	0.053	
-CHO	-0.001	+0.032	-0.029	+0.038	-0.014	+0.037	0.047	0.049	0.047
-COCH ₃	-0.007	+0.028	-0.036	+0.032	-0.020	+0.034	0.047	0.047	0.046
-CONH ₂	+0.005	+0.022	-0.024	+0.027	-0.009	+0.028	0.041	0.042	0.040
-COOH	+0.029	+0.034	+0.001	+0.037	+0.017	+0.036	0.044	0.046	0.043
-COF	+0.025	+0.036	-0.003	+0.040	+0.012	+0.039	0.045	0.047	0.044
-NO	+0.110	+0.037	+0.081	+0.044	+0.095	+0.040	0.054	0.057	0.053
-NO ₂	+0.227	+0.031	+0.198	+0.034	+0.213	+0.032	0.034	0.034	0.032
-CCH	+0.058	+0.005	+0.022	+0.011	+0.041	+0.012	0.047	0.046	0.043
-CN	+0.104	+0.022	+0.070	+0.027	+0.088	+0.026	0.043	0.044	0.041
-NC	+0.240	-0.018	+0.206	-0.014	+0.222	-0.012	0.035	0.032	0.030
-Li	-0.266	+0.092	-0.290	+0.091	-0.260	+0.094	0.059	0.064	0.064
-BeH	-0.215	+0.094	-0.240	+0.097	-0.215	+0.094	0.074	0.081	0.078
-BH ₂	-0.182	+0.106	-0.210	+0.113	-0.192	+0.108	0.082	0.090	0.086

^a q_σ and q_π are the total σ and π charges, respectively, donated to the ring by the substituent Z. ^b π_{R-Z} is the Mulliken overlap population of the adjacent π -type p orbitals in the bond joining Z to the ring. ^c From ref 24 unless otherwise noted. ^d Geometry optimized as described in text. ^e Planar bonds at N. ^f Pyramidal bonds at N.

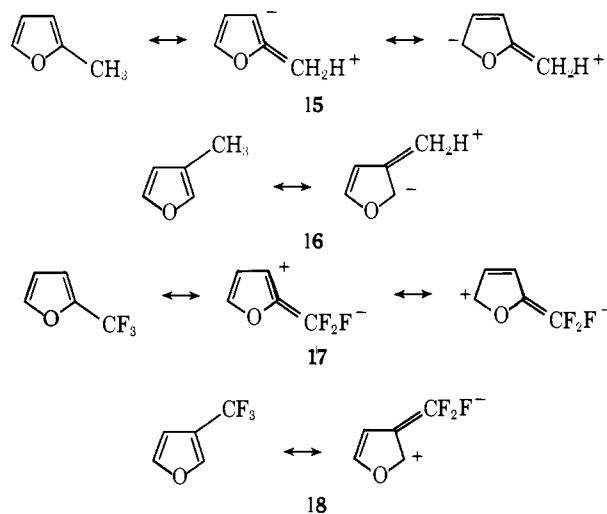
ents with X = CH₃, OH, and F are all found to be rotated out of the plane of the heterocyclic ring, a result which may be attributed to steric forces (X = CH₃) or hyperconjugation (X = OH and F).

For all the substituted methylfurans, with the exception of 2-trifluoromethylfuran, the stabilization energies for reaction 1 are calculated to be positive. It is of interest to attempt to correlate the stabilizing effect of the substituent in the 2 and 3 positions of furan with the σ - and π -electron donating nature of the substituent as measured by q_σ (B) and q_π (B) (Table III). Since both positions of the furan ring have greater π -electron density than is present in benzene, any π -electron-withdrawing substituent (i.e., one having a positive value of q_π (B)) will be expected, in the absence of other effects, to stabilize the furan ring more so than it will benzene, and thus to give rise to a positive value of ΔE_{SE} . The oxygen atom of the furan ring at the same time, however, will compete via an inductive effect with a σ -electron-withdrawing substituent, thus tending to destabilize relative to the corresponding benzene derivative those furan compounds where the substituent has a positive value of q_σ (B). Both these effects will be more pronounced at the 2 than at the 3 position owing to the greater π -electron density at the former position for the first effect and the closer proximity of the oxygen atom for the second. This electronic situation will be complicated by the respective steric environments of the substituent in the benzene and heteroaromatic rings and also by any dipole-dipole or hyperconjugative interactions.

The calculated stabilization energies (Table II) for this first group of molecules are found to be consistent with these intuitive predictions. Thus all the substituted methylfurans, with the exception of 2-trifluoromethylfuran, display a positive

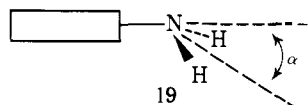
value of ΔE_{SE} for reaction 1. As in the case of the corresponding benzene series, the methyl and ethyl substituents have approximately the same stabilizing effect. As electronegative groups are attached to the methyl group, q_σ (B) becomes positive, competition with the heterocyclic oxygen is increased, and the stabilization energy decreases, actually becoming negative for 2-trifluoromethylfuran where the effect would be expected to be most pronounced.

The charge distributions in these molecules also show several interesting features, the effects being similar to the corresponding benzene derivatives.²⁴ Thus the π -charge distribution in the methylfurans (Figures 2 and 3) shows electron redistribution compatible with the valence structures shown as 15



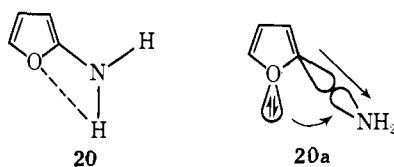
and **16**. This form of electron redistribution is reduced as the number of electronegative groups in the substituent is increased. For the trifluoromethylfurans a small π -electron withdrawal from the ring is predicted and the charge alternation within the ring is reversed (cf. **17** and **18**).

Furan-2- and -3-amine. Both furan-2-amine and furan-3-amine were considered with two distinct geometries. The standard geometric model²⁸ requires that the $-\text{NH}_2$ substituent be taken as planar trigonal if attached to an unsaturated atom as is the case here. However, experimental^{43,44} and theoretical²⁴ evidence for aniline suggests that the $-\text{NH}_2$ group is nonplanar when attached to a benzene ring. A second geometry was therefore considered for both molecules in which the bond angles at nitrogen were kept equal (i.e., local C_{3v} symmetry at N), but allowed to vary from 120° . Optimization in this manner leads to out-of-plane angles (α , cf. **19**) of 51.2

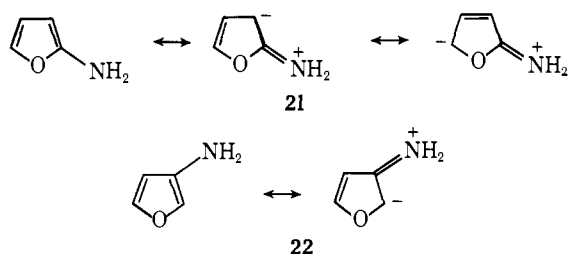


and 51.4° , HNH angles of 110.8 and 110.8° , and inversion barriers of 15.5 and 16.7 kJ mol^{-1} for the furan-2- and -3-amines, respectively. These values correspond to a greater degree of nonplanarity at nitrogen than in aniline itself ($\alpha = 47.7^\circ$) and are consistent with less effective interaction of the amino lone pair with the furan compared with the benzene nucleus. The absolute values of the inversion barriers are likely to be overestimated in the light of results of previous work with the STO-3G basis set.^{24,25}

Stabilization energies for furan-3-amine are calculated to be strongly negative, consistent with the π -electron-donating, σ -electron-withdrawing nature of the substituent. For furan-2-amine, on the other hand, ΔE_{SE} is close to zero for the planar structure and is slightly positive when the bonds at nitrogen are allowed to become pyramidal. Clearly, there must be compensating stabilizing effects in this case. One possibility is intramolecular hydrogen bonding (**20**). Another is *in-plane* hyperconjugative interaction of the oxygen in-plane lone pair with the C-N bond (**20a**).

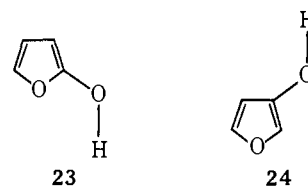


The π -electron distributions are consistent with contributions from the expected valence structures as shown in **21** and **22**. Both molecules display an increased π -electron density on



the ring oxygen, relative to unsubstituted furan. The π -electron donation from the amino group apparently has the effect of suppressing electron delocalization from the oxygen.

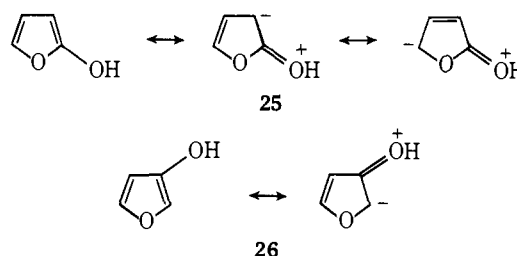
Furan-2-ol, Furan-3-ol and Related Molecules: FuOX, X = H, CH₃, and F. Furan-2-ol is predicted to assume a planar cis conformation (**23**), this resulting in a more favorable antiparallel alignment of the component dipole moments. A planar trans structure (**24**) is slightly favored for furan-3-ol, but this result may be reversed in a more sophisticated treatment. For a related model system, vinyl alcohol, geometry optimization



is found^{46,47} to be important in reproducing the experimentally observed⁴⁸ preference for an $\text{HOC}=\text{C}$ syn conformation.

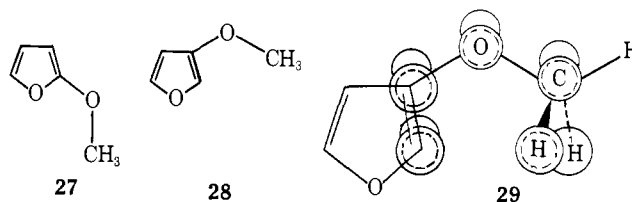
The barrier to rotation in both molecules (ca. 10 kJ mol^{-1}) is smaller than the corresponding barrier (21.5 kJ mol^{-1}) for phenol.²⁴ A comparison of the π $\rho_{\text{H-X}}$ overlap populations reveals a smaller degree of C-O double bond character in phenol than in the furanols. These results are all consistent with the opposing π -electron effects of the furan ring and the hydroxy substituent. They are also reflected in a large negative stabilization energy for furan-3-ol. For the 2-hydroxy compound, ΔE_{SE} is positive, which means that, as for furan-2-amine, there must be factors compensating for the unfavorable positive q_σ and negative q_π of the substituent. Possibilities in this case include the favorable antiparallel alignment of dipoles, intramolecular H bonding in **23**, and hyperconjugative interaction with the in-plane lone pair on the ring oxygen in a manner analogous to **20a**.

The π -electron populations for the furanols show π -electron donation to the ring consistent with the valence structures shown in **25** and **26**. There is increased π -electron density on



the heterocyclic oxygen relative to furan itself owing to the inhibition of electron delocalization from that atom by the presence of the strong π -donor substituent.

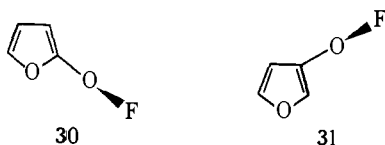
The decreased steric interaction with the furan ring compared with benzene is seen in the preference for planar over orthogonal conformations of 2- and 3-methoxyfuran, whereas for anisole, with standard geometry, an orthogonal structure was found²⁴ to have a lower energy. Optimization of the COC angle in 2-methoxyfuran shows the cis structure (**27**) to be slightly favored over the trans. Again this conformation maintains the more favorable orientation of intramolecular dipoles. 3-Methoxyfuran reverses the preference of its hydroxy



analogue, adopting instead a planar cis conformation (**28**). The significantly higher energy of the trans form cannot be accounted for in terms of steric repulsions since a comparison of interatomic distances shows that these are similar in both species. However, the cis conformation (**28**) incorporates the favored arrangement about the C-O bond found in methyl vinyl ether, i.e., C-O eclipsing the double bond.^{46,49,50} This conformation would also benefit from 6π -electron cyclic stabilization (cf. **29**).^{51,52} Stabilization energies for the methoxyfurans are more positive (2-compound) or less negative (3-compound) than for the corresponding furanols. These results probably reflect the steric crowding in the anisole refer-

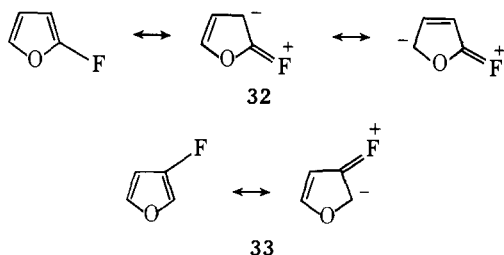
ence rather than a special stabilizing effect in the methoxyfurans.

In contrast to the situation for phenyl hypofluorite, where a lower energy is found for a planar compared with an orthogonal conformation,^{24,53} orthogonal structures (**30**, **31**) are



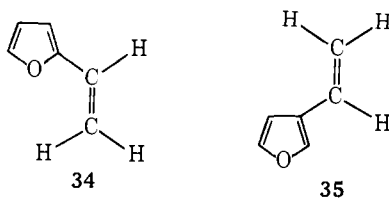
found to be preferred by both furan-2- and furan-3-hypofluorite. The calculated F...H and F...O interatomic distances in the planar forms are less than the sum of the van der Waals radii for the respective atoms and so some steric crowding can be predicted. However, this is also likely to be the case, probably even more so, in phenyl hypofluorite. A more compelling explanation for the conformational behavior comes by noting that the unfavorable π -donor and σ -acceptor properties of the OF substituent are markedly reduced in going from a planar to an orthogonal structure. Thus *cis*- and *trans*-furan-2-hypofluorite have $q_\sigma = +0.19$, $q_\pi = -0.086$ compared with $q_\sigma = +0.146$, $q_\pi = -0.010$ in the orthogonal structure. Likewise, *cis*- and *trans*-furan-3-hypofluorite have $q_\sigma = +0.205$, $q_\pi = -0.079$ compared with $q_\sigma = +0.161$ and $q_\pi = -0.008$ in the orthogonal structure. While the planar structures of the other molecules in this section show similar values for q_σ and q_π , rotation to an orthogonal form does not produce the large change that is found for the hypofluorites. The large decrease in π donation to the ring in the orthogonal hypofluorites may be due to competing hyperconjugative electron withdrawal by the O-F bond. In the case of furan-2-hypofluorite, the planar structures are further destabilized by unfavorable dipole interactions.

2- and 3-Fluorofuran. The fluoro substituent is a strong σ -electron acceptor and a π -electron donor. Both these properties are unfavorable in the furan ring and this is reflected in a negative ΔE_{SE} for 3-fluorofuran. For 2-fluorofuran, we again invoke in-plane hyperconjugative stabilization (cf. **20a**) to explain the positive ΔE_{SE} . The charge distributions reflect electron delocalization of the type **32** and **33**. Once again, the



π -electron-donating substituent suppresses, to some extent, π -electron donation from the ring oxygen.

2- and 3-Vinylfuran. For 2- and 3-vinylfuran, lowest energies are found for planar *cis* (**34**) and *trans* (**35**) structures, respectively. Optimization of the CCC angle in the 2-compound

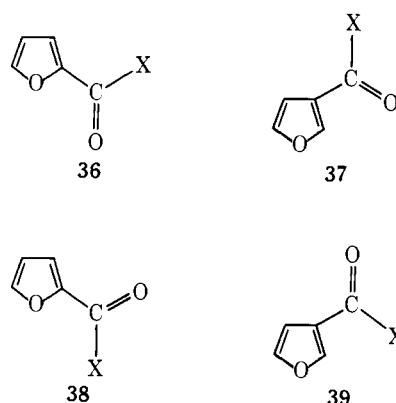


leads to a widening of 4-5° for all conformations but has only a small effect on relative energies; the *trans*-*cis* energy difference is reduced slightly to 2.2 kJ mol⁻¹.

The vinyl substituent in styrene is calculated²⁴ to be a very mild σ - and π -electron acceptor: $q_\sigma(\text{B}) = +0.003$, $q_\pi(\text{B}) = +0.006$. The effect of the furan ring is to induce the vinyl group

to become a stronger σ -electron donor, particularly in the 2 position, where $q_\sigma = -0.029$. Both the 2- and 3-vinylfurans are significantly stabilized with ΔE_{SE} values of +29.1 and +16.6 kJ mol⁻¹, respectively. Part of this increased stabilization is, of course, due to the diminished steric interaction in the planar forms of the vinylfurans compared with styrene and the ΔE_{SE} values are substantially reduced (to 18.5 kJ mol⁻¹ for 2-vinylfuran) as a result of partial geometry optimization for both styrene and the vinylfuran. The barrier to internal rotation (Table I) is slightly greater for 2-vinylfuran than that calculated either for 3-vinylfuran or for styrene²⁴ (18.5 kJ mol⁻¹ with partial optimization) suggesting greater conjugation at the 2 than at the 3 position. This is borne out by the π -overlap populations (Table III) for the respective C-C bonds. As for styrene,²⁴ the vinyl substituent in furan does not significantly modify the π -electron distribution in the ring.

2- and 3-Carbonylfurans: FuCOX, X = H, CH₃, NH₂, OH, and F. The carbonyl-substituted furans have attracted considerable interest in the literature.⁵⁴⁻⁷⁴ In this section, we consider the series FuCOX with X = H, CH₃, NH₂, OH, and F in *cis* (**36**, **37**), *trans* (**38**, **39**), and orthogonal conformations.



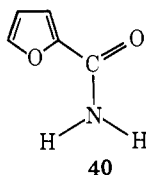
As for the vinyl substituent, the carbonyl group conjugates most effectively with the furan ring in the planar conformations. It would be expected therefore that these structures should be stabilized relative to the orthogonal forms if steric interactions are unimportant. Indeed, we find (Table I) a strong preference for the planar conformations for all the 2- and 3-substituted carbonylfurans. For the 2-substituted furans, there is normally a distinct preference for either a *cis* or *trans* structure. On the other hand, for the 3-substituted furans the calculated energy difference between the *cis* and *trans* structures is extremely small and probably below the level of significance of our approach. Our previous calculations for furan-3-carbaldehyde showed that this energy difference remains small even with extensive geometry optimization. The barriers to rotation in the 3-carbonylfurans are approximately the same as those calculated for the corresponding benzene derivatives except in those cases (acetophenone and benzamide in particular) where steric interactions led to an underestimation of the rotational barrier in the substituted benzene. It should be noted that the energy of the orthogonal structure (i.e., $\theta = 90^\circ$) only provides a good estimate of the rotational barrier for those molecules for which the *cis*-*trans* energy difference is small.

Furan-2-carbaldehyde has been discussed in detail in a previous paper.^{23,54} Our calculations here using a slightly different model yield results similar to those obtained previously.²³ The *trans* conformation (**38**, X = H) is favored by 4.1 kJ mol⁻¹ over the *cis* structure (**36**, X = H). This agrees with gas-phase experimental data^{56,57} which yield values of 3.1 and 8.5 kJ mol⁻¹ for the *cis*-*trans* energy difference. Our calculated barrier to rotation from the *cis* structure (ca. 24.7 kJ mol⁻¹) compares with experimental values^{56,57} of 36 and

25 kJ mol⁻¹. We note that in media of high relative permittivity ($\epsilon_r > \text{ca. } 3$), the cis conformation becomes favored.^{55,58}

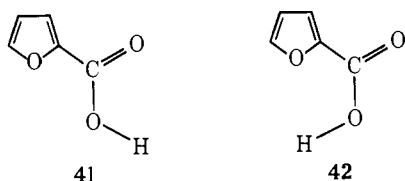
2-Acetylfuran is also found to show a significant preference (5.0 kJ mol⁻¹) for the trans form (**38**, X = CH₃), consistent with the dipole moment and Kerr constant results in nonpolar solvents.^{55,59} Data from NMR investigations,⁶⁰⁻⁶⁵ on the other hand, strongly suggest that the cis isomer is favored in polar solvents. It seems likely, therefore, that for 2-acetylfuran, as for furan-2-carbaldehyde, reaction field stabilization of the more dipolar cis form takes place in polar solutions, giving rise to a change of conformational preference for the molecule. The respective energies for the orthogonal structures of the formyl and acetyl derivatives suggest a lower barrier for 2-acetylfuran, as found experimentally.⁶⁰ It has been suggested⁶⁰ that the CH₃ substituent decreases the ability of the COX (X = H) group to conjugate with the ring. This is supported by the results in Table III, which show a decrease in the π -overlap population for the C(2)-C bond and also a decrease in the extent of π -electron acceptance by the substituent. Unfavorable steric interaction in planar structures of acetylfurans compared with furancarbaldehydes would also lead to decreased barriers.

Furan-2-amide has been observed experimentally to be planar.⁶⁶ Our calculations show a strong (11.1 kJ mol⁻¹) preference for the planar trans (**40**) over the planar cis con-



formation. This structure has a significantly more favorable alignment of the large component dipoles and would also be favored by intramolecular hydrogen bonding.

For furan-2-carboxylic acid, the energy difference between the cis and trans isomers is not very great with a slight preference for the trans structure **41**. Additional calculations were



carried out with OCOH trans (as opposed to OCOH cis in the standard orientation) because of the possibility of intramolecular hydrogen bonding. This structure (**42**) is found to lie 3.0 kJ mol⁻¹ above **41**. The x-ray crystal structures of the furan-2-carboxylic^{67,68} and -2,5-dicarboxylic⁶⁹ acids both have OCC=O cis but this result is undoubtedly influenced by intermolecular hydrogen bonding and other solid-phase effects. A CNDO/CI investigation of furan-2-carboxylic acid has also been carried out⁷⁰ on an assumed conformation **42**.

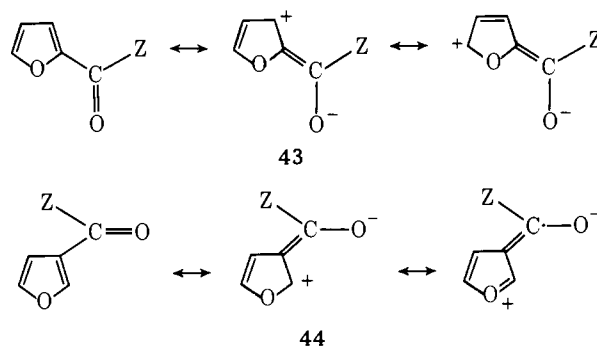
Furan-2-carbonyl fluoride is calculated to be planar trans (**38**, X = F) with a small energy difference between this and the cis form, in agreement with the tentative conclusions of an IR and NMR spectral study.⁷¹ Experimental results for furan-2-carbonyl chloride^{64,72-74} also suggest a small energy difference between the planar conformations of that molecule.

The rotational barriers are found to be higher for substituents in the 2 position than those for the substituted benzenes or 3-furan derivatives, suggesting greater interaction between the substituent group and the heterocyclic ring in the former position. This enhanced conjugation is mirrored also in the larger π -overlap population for the C(2)-C bond, and is con-

sistent with the π -electron-withdrawing character of these substituents coupled with the larger π density at the 2 position.

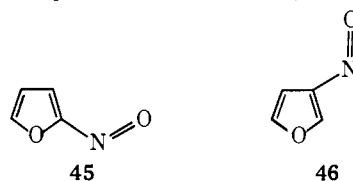
The stabilization energies of the carbonylfurans show interesting correlations with the q_σ charges of the substituents. Thus the molecules with X = H, CH₃, and NH₂, having small values of q_σ (B) and large positive values of q_π (B), produce the expected stabilization of the furan ring with respect to benzene. The effect is more pronounced for substituents in the 2 position, the furan oxygen inducing the substituents to surrender more σ electronic charge, thus producing more negative values of q_σ . Both the carboxylic acid and the carbonyl fluoride derivatives are calculated to have large positive values of q_σ (B) (+0.029 and +0.025, respectively), by virtue of the electronegativity of the OH and F groups. Consequently they compete with the heterocyclic oxygen for the σ charge; the stabilization energy is considerably reduced for the 3-substituted furans, and changes sign for the 2-furan derivatives, where the competing groups are closest.

The calculated charge distributions all show withdrawal of π electrons from the ring in accordance with contributions from the valence structures shown (for cis conformations) in **43** and



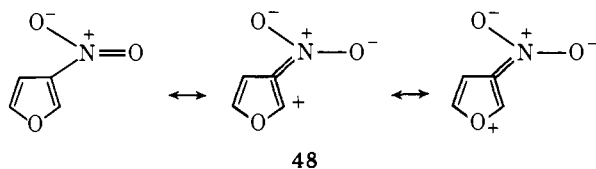
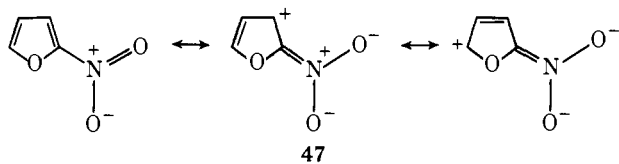
44. Enhanced π -electron donation from the ring oxygen does not appear to occur for the 2-substituted compounds but it does occur to a small extent for the 3 derivatives.

2- and 3-Nitrososfuran. Both 2- and 3-nitrososfuran show a preference for the planar trans structures (**45**, **46**) having large



barriers to rotation to the orthogonal forms. In **45**, this may be attributed to a more favorable alignment of component dipoles, while in **46** the trans diene arrangement may be the driving force. The stabilization energies are both distinctly positive despite the tendency for σ -electron withdrawal (q_σ (B) = +0.110). Clearly this effect is counterbalanced by a stabilizing π -electron-withdrawal capacity, demonstrated by the considerable π -overlap population in the C-N bond. In the orthogonal conformations, the nitroso group becomes π -electron donating (q_π = -0.021 and -0.019 for the 2 and 3 compounds, respectively), leading to a high energy for these structures. The same effect was noted²⁴ for nitrosobenzene and manifests itself in a reversed charge alternation (see Figures 2 and 3).

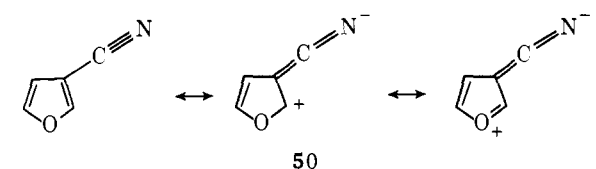
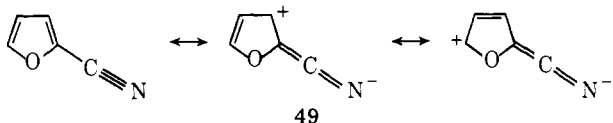
2- and 3-Nitrofuran. As with nitrobenzene, 2- and 3-nitrofuran are predicted to adopt planar configurations. The barriers to internal rotation are somewhat reduced from the calculated value (24.0 kJ mol⁻¹) for nitrobenzene, suggesting destabilization of the planar structures. The nitro group has a very high σ -electron-withdrawing capacity (q_σ (B) = +0.227) and both furan species are consequently strongly destabilized relative to nitrobenzene. π -Electron redistribution



is consistent with **47** and **48**. Again, further electron delocalization from the ring oxygen is induced by the π -electron-withdrawing substituent when in the 3 position but not in the 2 position.

2- and 3-Ethynyl-, -Cyano-, and -Isocyanofuran. These six molecules with triply bonded substituents follow the pattern of the corresponding benzene derivatives. Thus both the ethynyl and the cyano substituents are calculated to withdraw σ and π electrons from the ring. The cyano group has the greater tendency to compete with the ring oxygen for σ electrons, and consequently the stabilization energy of 3-cyanofuran relative to the corresponding substituted benzene is lower than that of 3-ethynylfuran. In 2-cyanofuran, the competition for σ electrons is enhanced,⁷⁵ and consequently a destabilization relative to benzonitrile is predicted. The two isocyanofurans have an even larger σ -electron-withdrawing ability, coupled with a tendency to donate π electrons into the ring. Accordingly, negative values of ΔE_{SE} are obtained for both 2- and 3-isocyanofuran.

The π -charge distributions for the cyanofurans are consistent with the valence-bond resonance structures shown in **49** and **50**.



Furan with Electropositive Substituents: FuX, X = Li, BeH, and BH₂. The substituents Li, BeH, and BH have been studied in detail by Pople, Schleyer, and co-workers⁷⁶ and are characterized as being σ -electron donors and π -electron acceptors. As such, they should be ideally suited for stabilizing the furan nucleus. Indeed, we find large positive values of ΔE_{SE} (Table II) in each case for both the 2- and 3-substituted furans. Largest values occur for the Li substituent reflecting the importance of its σ -electron donating ability.

Conclusions

Several important general conclusions can be drawn from this ab initio molecular orbital study of the 2- and 3-substituted furans.

(1) The furyl group prefers to act, relative to phenyl, as a π -electron donor and a σ -electron acceptor. Inductive σ -electron withdrawal by the ring oxygen is more pronounced at the 2 position. At the same time, the π -electron distributions show enhanced π -electron density at the 2 position compared with the 3 position both overall and in the highest occupied molecular orbital.

(2) As a consequence and in the absence of other interac-

tions, furan is stabilized by substituents which are π -electron acceptors and σ -electron donors and destabilized by substituents which are π -electron donors and σ -electron acceptors. These effects are greater at the 2 than at the 3 position.

(3) Several additional stabilizing or destabilizing mechanisms are operative for 2-substituted furans. These include (a) hyperconjugative interaction of the in-plane lone pair on the oxygen with the C-X bond at the 2 position for an electronegative substituent X; (b) intramolecular hydrogen bonding; (c) dipolar interactions; and (d) steric effects.

(4) The preference for planar vs. orthogonal structures is generally determined by conjugative and hyperconjugative vs. steric interactions. However, steric effects are found to be less important in furans than in corresponding substituted benzenes.

(5) The preference between cis and trans planar structures can generally be rationalized in terms of (a) the tendency of a single bond of the substituent to eclipse a double bond (C2-C3) of the furan ring; (b) the tendency for antiparallel alignment of component dipoles; and (c) the stabilizing effect of intramolecular hydrogen bonding.

(6) The fact that the carbon-carbon bonds in furan can be distinguished as having more (C2-C3) and less (C3-C4) double bond character manifests itself in conformational preferences for 3-substituted furans (cf. 5 (a) above) which do not exist in substituted benzenes.

(7) Calculated π -electron distributions are consistent with contributions from the expected valence structures. Delocalization from the ring oxygen is enhanced by π -electron-withdrawing substituents in the 3 position but not in the 2 position. Since the furan ring is a π -electron donor and a σ -electron acceptor, q_σ values in the substituted furans are found to decrease and q_π values to increase relative to the values in corresponding substituted benzenes.

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References and Notes

- (a) A. P. Dunlop and F. N. Peters, "The Furans", Reinhold, New York, N.Y., 1953; (b) P. Bosshard and C. H. Eugster, *Adv. Heterocycl. Chem.*, **7**, 378 (1966); (c) S. F. Mason, *Phys. Methods Heterocycl. Chem.*, **2**, 1 (1963); (d) R. F. M. White, *ibid.*, **2**, 103 (1963); (e) A. P. Ambler, *ibid.*, **2**, 165 (1963).
- H. H. Jaffé and H. L. Jones, *Adv. Heterocycl. Chem.*, **3**, 209 (1964).
- G. Marino, *Adv. Heterocycl. Chem.*, **13**, 235 (1971).
- J. M. Angelelli, A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, **28**, 2037 (1972).
- M. Sénéchal and P. Saumagne, *C. R. Acad. Sci., Ser. B*, **276**, 79 (1973).
- S. Gronowitz, I. Johnson, and A. B. Hornfeldt, *Chem. Scr.*, **7**, 211 (1975).
- A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961.
- M. K. Orloff and D. D. Fitts, *J. Chem. Phys.*, **38**, 2334 (1963).
- L. Pajol and A. Julg, *Theor. Chim. Acta*, **2**, 125 (1964).
- N. Solony, F. W. Birss, and J. B. Greenshields, *Can. J. Chem.*, **43**, 1569 (1965).
- P. J. Black, R. D. Brown, and M. L. Heffernan, *Aust. J. Chem.*, **20**, 1325 (1967).
- R. Phan-Tan-Luu, L. Bouscasse, E. J. Vincent, and J. Metzger, *Bull. Soc. Chim. Fr.*, 3283 (1967).
- W. Adam and A. Grimison, *Theor. Chim. Acta*, **7**, 342 (1967).
- D. T. Clark, *Tetrahedron*, **24**, 3285 (1968).
- M. Jungen and H. Labhart, *Theor. Chim. Acta*, **9**, 345 (1968).
- F. Momicchioli and G. Del Re, *J. Chem. Soc. B*, 674 (1969).
- F. Török, A. Hegedüs, and P. Pulay, *Theor. Chim. Acta*, **32**, 145 (1973).
- A. Bohmik, S. Bhattacharyya, and R. Basu, *Indian J. Chem.*, **13**, 555 (1975).
- H. Preuss and R. Janoschek, *J. Mol. Struct.*, **3**, 423 (1969).
- M. H. Palmer and A. J. Gaskell, *Theor. Chim. Acta*, **23**, 52 (1971).
- M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, **26**, 357 (1972).
- P. Siegbahn, *Chem. Phys. Lett.*, **8**, 245 (1971).
- (a) I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1601 (1977); (b) C. Petrongolo, *Chem. Phys. Lett.*, **42**, 512 (1976).
- W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).
- W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana Uni-

- versity, Bloomington, Ind.
- (26) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (27) D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975).
- (28) (a) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967); (b) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *ibid.*, **98**, 1663 (1976); (c) *ibid.*, **97**, 3402 (1975); (d) We use C3-B3 = 1.54 Å, C3-Be2 = 1.69 Å, and C3-Li1 = 2.01 Å.
- (29) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).
- (30) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
- (31) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 289 (1971).
- (32) L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).
- (33) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
- (34) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup Anderson, and M. Shottländer, *J. Mol. Spectrosc.*, **9**, 124 (1962).
- (35) M. H. Sirvetz, *J. Chem. Phys.*, **19**, 1609 (1951).
- (36) W. G. Norris and L. C. Krisher, *J. Chem. Phys.*, **51**, 403 (1969).
- (37) T. Ogata and K. Kozima, *Bull. Chem. Soc. Jpn.*, **44**, 2344 (1971).
- (38) W. J. Hehre and L. Salem, *J. Chem. Soc., Chem. Commun.*, 754 (1973).
- (39) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).
- (40) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968).
- (41) (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 6380 (1970); (b) *ibid.*, **92**, 6987 (1970); (c) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972).
- (42) A. A. Hasanein and S. Kovac, *Collect. Czech. Chem. Commun.*, **39**, 3613 (1974).
- (43) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).
- (44) J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectrosc.*, **20**, 359 (1966).
- (45) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
- (46) S. Samdal and H. M. Seip, *J. Mol. Struct.*, **28**, 193 (1975).
- (47) W. J. Bouma and L. Radom, *J. Mol. Struct.*, **43**, 267 (1978).
- (48) S. Saito, *Chem. Phys. Lett.*, **42**, 399 (1976).
- (49) (a) N. L. Owen and N. Sheppard, *Trans. Faraday Soc.*, **60**, 634 (1964); (b) P. Cahill, L. P. Gold, and N. L. Owen, *J. Chem. Phys.*, **48**, 1620 (1968).
- (50) I. G. John and L. Radom, *J. Mol. Struct.*, **36**, 133 (1977).
- (51) D. Cremer, J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 6900 (1974).
- (52) F. Bernardi, N. D. Epitios, R. L. Yates, and H. B. Schlegel, *J. Am. Chem. Soc.*, **98**, 2385 (1976).
- (53) The STO-3G energy for orthogonal PhOF is -399.125 96, i.e., 5.5 kJ mol⁻¹ above the planar form.
- (54) For a summary of the main references to studies of furan-2-carbaldehyde, see ref 55 (to 1973) and 23 (since 1973).
- (55) C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J. Chem. Soc., Perkin Trans. 2*, 744 (1975).
- (56) F. Mönnig, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch. A*, **20**, 1323 (1965); **21**, 1633 (1966).
- (57) F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta, Part A*, **23**, 891 (1967).
- (58) R. J. Abraham and T. M. Siverns, *Tetrahedron*, **28**, 3015 (1972).
- (59) V. N. Sheinker, A. S. Kuzharov, S. N. Nazarova, and O. A. Osipov, *Zh. Org. Khim.*, **11**, 1520 (1975).
- (60) L. Arlinger, K. I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, **24**, 662 (1970).
- (61) M. L. Martin, J. C. Roze, G. J. Martin, and P. Fournai, *Tetrahedron Lett.*, 3407 (1970).
- (62) S. Nagata, T. Yamabe, K. Yoshikawa, and H. Kato, *Tetrahedron*, **29**, 2545 (1973).
- (63) K. I. Dahlqvist and A. B. Hörnfeldt, *Tetrahedron Lett.*, 3837 (1971).
- (64) D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Lett.*, 3183 (1974).
- (65) B. Roques, S. Combrisson, and F. Wehlri, *Tetrahedron Lett.*, 1047 (1975).
- (66) R. G. Quinones, J. L. Fernandez, and H. Kelling, *Sobre Deriv. Cana Azucar*, **6**, 47 (1972); *Chem. Abstr.*, **78**, 146948x (1973).
- (67) H. T. Goodwin and M. C. Thompson, *Acta Crystallogr.*, **7**, 166 (1954).
- (68) P. Hudson, *Acta Crystallogr.*, **15**, 919 (1962).
- (69) E. Martuscelli and C. Pedone, *Acta Crystallogr., Sect. B*, **24**, 175 (1968).
- (70) C. Decoret and B. Tinland, *Gazz. Chim. Ital.*, **101**, 502 (1971).
- (71) D. J. Chadwick, *Tetrahedron Lett.*, 679 (1975).
- (72) V. N. Sheinker, A. S. Kuzharov, D. Y. Movshovich, Z. N. Nazarova, V. A. Piven, and O. A. Osipov, *Zh. Obshch. Khim.*, **45**, 884 (1975).
- (73) C. Pigenet, J. P. Morizur, Y. Pascal, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 361 (1969).
- (74) G. Cassanas-Fabre, *J. Mol. Struct.*, **25**, 281 (1975).
- (75) L. W. Deady, R. A. Shanks, and R. D. Topsom, *Tetrahedron Lett.*, 1881 (1973).
- (76) See ref 28b and references cited therein; also J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 1 (1977).

Hydrogen Bonding in Pure and Aqueous Formamide

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Abstract: An extension of a recent study on the structure of liquid and aqueous formamide has been made using ab initio SCF computations and approximate calculations of proton shifts. The results, compared with the available ESCA, NMR, and dielectric constant data, seem to indicate that the dominant unit in the structure of liquid formamide is one that contains a cyclic dimer and linear chain held together by hydrogen bonds. Further evidence is presented for the structure of hydrated formamide consistent with the original model of four water molecules in the primary hydration sphere.

In a recent paper,^{2a} tentative models for the structure of liquid and aqueous formamide have been proposed on the basis of ab initio SCF computations on various polymers and polyhydrates. Further computations and reexamination of all the results in connection with the available experimental NMR, ESCA, and dielectric evidence lead to a partially modified description of these systems.

Computational Details

The supplementary SCF computations have been performed as in ref 2a using an STO-3G basis set but modified version^{2b} of the original QCPE program.³

For the computation of the variations of the chemical shifts we have used a procedure described earlier.^{4,5} In these calculations the variation of the chemical shift of a proton of a molecule A due to the interaction with a molecule B is ap-

proximated by a sum of two terms: the local magnetic anisotropy contribution and the polarization effect.⁶ For the first term we calculate the magnetic field created at the studied proton of A by the magnetic susceptibility tensors of all the atoms of molecule B through the dipolar approximation.⁷⁻⁹ (Another procedure developed by Barfield et al.¹⁰ cannot be used here since the experimental values of the principal components of the shielding tensors are not available, to our knowledge, for nitrogen and oxygen atoms of amides.)

For a proton P of molecule A the magnetic term is given by

$$\sum_Q \Delta\delta_{Q(B)}^P(A) \quad (1)$$

with the summation running over all the atoms of molecule B.