Non-linear Optical Properties of Organic Molecules. Part 3.† Effect of Substituents on the Calculated Hyperpolarisability of Monosubstituted Benzenes

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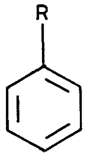
The hyperpolarisabilities of a range of substituted benzenes have been calculated using a modified CNDO/2-CI method. The values obtained have been rationalised in terms of ground- and excited-state π-charges at the aromatic ring. It is shown that the effect of electron donors and attractors is generally enhanced relative to their behaviour in the corresponding ground state. Of the substituents studied, the NMe_2 group is calculated to be the most powerful electron-donating group and that the CHO, NO_2, and NO groups are the most effective electron attractors.

The molecular hyperpolarisability (β_{ijk}) of a large number of organic compounds has been evaluated both experimentally using Electric Field Induced Second Harmonic Generation in solution (EFISH) and theoretically using either the sum-over-states or finite field molecular orbital methods.[1] However, to date, no systematic appraisal of the influence of substituents on the β values for a given molecular system has been attempted though generally it has been established that the greatest values are obtained for molecules which contain powerful electron donors and attractors at either end of a suitable conjugated pathway. While a previous paper deals with the nature of the conjugated pathway between donor and acceptor groups,[2] this work is concerned with an examination of the effects of simple substituents on the calculated hyperpolarisability of monosubstituted benzenes (I) in an endeavour to produce an order of substituent constants which would be useful for predictive purposes and transferable to other conjugated systems.



(I)

All calculations reported here were carried out with the CNDOVSB method[3] which involves an initial configuration interaction treatment of ground- (g) and excited-state (n and n') wavefunctions and then evaluation of the hyperpolarisability tensor from the improved wavefunctions using expression (1)[4] where $r^i_{gn} = \langle g|r^i|n\rangle$, $r^i_{nn} = \langle n'|r^i|n\rangle$, ω_{ng} is the eigenvalue of ψ_n, relative to the ground state (the electronic transition energy), e is the magnitude of the electronic charge, and ω is the frequency of the applied radiation field. All components of the tensor are calculated, but the most relevant quantity, which relates to the experimental data from EFISH measurements, is the vector component, β_x, defined by equation (2) where x is aligned along the direction of the dipole moment, and y lies in the molecular plane.

$$\beta^{2\omega}_{ijk} + \beta^{2\omega}_{ikj} = (-e^3/4\hbar^2) \times \sum_{n'}\sum_{n}\Bigg\{(r^j_{gn'}r^i_{n'n}r^k_{ng} + r^k_{gn'}r^i_{n'n}r^j_{ng})\left[\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right] + (r^i_{gn'}r^j_{n'n}r^k_{ng} + r^i_{gn'}r^k_{n'n}r^j_{ng})\left[\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}\right] + (r^j_{gn'}r^k_{n'n}r^i_{ng} + r^k_{gn'}r^j_{n'n}r^i_{ng})\left[\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right]\Bigg\} \quad (1)$$

$$\beta_x = \beta_{xxx} + 1/3\Sigma(\beta_{xii} + 2\beta_{iix}) \quad (2)$$

In conjugated systems, β_x is derived mainly from transition moments between π-orbitals only and for the monosubstituted benzenes a limited number of excited states contribute to most of its value (see below).

It follows that a picture of the change in π-electron distribution in the aromatic ring on excitation for a given substituent should lead to a greater understanding of the electronic factors which contribute to the calculated β_x values. At the present time, the substituent constant, $\sigma_R{}^o$, has often been used to measure the relative efficacy of substituents in terms of their ability to attract or donate π-electrons.[5] Furthermore, it has been established that the $\sigma_R{}^o$ value of a given substituent is directly proportional to the calculated ground-state π-electron charge (q) in the aromatic ring using relation (3)[5] where K is a constant. Thus nitro and cyano groups are calculated to be powerful π-electron attractors and amino and hydroxy groups are π-electron donors. However, this classification is only satisfactory as an aid to the interpretation of ground-state properties and any correlation with excited states must be considered fortuitous. In the present studies, the excited-state charges have been

$$\sigma_R{}^o = K\Sigma q \quad (3)$$

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† Part 2, preceding paper.

calculated for the dominant excited states and used to derive a series of excited-state substituent constants.

Results and Discussion

All the molecules calculated in the present studies were constructed using molecular graphics from a standard benzene ring with all angles at 120° and C–C and C–H bond lengths of 1.40 and 1.08 Å, respectively. The substituents were placed in the plane of the aromatic ring using standard bond lengths and angles[6] except for the geometry of the nitroso group which was taken from the crystal structure of 2,4-bis-(*NN*-dimethylamino)nitrosobenzene[7] and the nitro group which was based on the crystal structures of 4-nitroaniline[8] and 4-nitroanisole.[9] Initially, the nitrogen atom of aniline and *NN*-dimethylaniline and the oxygen atom of phenol and anisole were assumed to be sp^2 in character.

The results show, as expected, that π-electron donors or acceptors have the greatest effect and σ-bonded substituents such as CH_3 or CF_3 have the least. A comparison between the calculated and experimental β_x results obtained from EFISH measurements, where available,[1] shows a reasonable correlation on the whole for electron attractors such as the NO_2 and CN groups but a poor correlation for electron donors such as the NH_2, NMe_2, and OH groups which have higher values than expected (Table 1). This apparent discrepancy, however, is resolved when the selected conformations for these groups are changed. An examination of crystallographic data shows that aniline is tetrahedral (sp^3 nitrogen) in the solid state[10] and a subsequent calculation on this structure gives a reduced β_x value (0.54 *versus* 3.83) which is more consistent with the range of experimental results (Table 1). It seems likely, therefore, that the high β_x values calculated for the anilines and phenols is a result of the sp^2 conformations selected and that the molecules are mainly tetrahedral in solution under the conditions of measurement. An assessment of the full influence of the substituents on a conjugated system, however, can only be realised if they are calculated in the trigonal sp^2 conformation as described above (Table 1) which arises when the substituent interacts with another group. For example, the tetrahedral sp^3 nitrogen of the amino-group of aniline changes to a trigonal sp^2 conformation in 4-nitroaniline.[8]

The calculated results also show that in some cases other vector components of the tensor have greater values than that (β_x) which lies in the direction of the molecular dipole. Thus the hyperpolarisability of anisole, phenol, and benzaldehyde is greatest for the *y* component and that for tetrahedral aniline is greatest for the *z* component. These apparent anomalies arise because the major contribution to the dipole moment is derived from the internal polarisation of the substituent group rather than its interaction with the aromatic ring. Thus the dipole moment of benzaldehyde contains a significant contribution from the in-plane C=O dipole and that for tetrahedral aniline contains a contribution from the out-of-plane N–H dipole. The experimental β_x results derived from EFISH measurements may therefore seriously underestimate the intrinsic hyperpolarisability of a given molecular system as the molecule is orientated along the dipole moment by the applied direct current field and not along an axis which produces the maximum interactions between the subsitituent and the aromatic ring.

The calculated dipole moments shown (Table 1) are generally overestimated in the ground state and underestimated in the dominant excited state relative to the experimental measurements[11] though a better correlation is observed with the transition energies.[12] These results reflect the parameterisation scheme originally selected for the CNDOVSB method which attempted to provide the best fit between the calculated and experimental ground-state dipole moments on the one hand and the electronic transition energies on the other for a series of representative molecules.[3]

A comparison of the ground- (q_g) and excited-state charge distributions for the first major excited state (q_e) summed over all the atoms of the aromatic ring is shown in Table 2. Overall, the semiempirical method gives a reasonable description of the total ground-state charges when compared with the published results from more accurate STO-3G calculations[13] although there is considerable variation in the magnitude of the charge. Because the geometries selected for these calculations sometimes differ from those reported, the *ab initio* work has been repeated at the STO-3G and also at the 3-21G level. Additionally the calculations on nitrobenzene have been carried out on both a standard structure (with an Ar–NO_2 distance of 1.40 Å) and that derived from experimental geometries to compare with published work. The results show few differences between the

Table 1. Calculated hyperpolarisabilities, dipole moments, and spectroscopic data for monosubstituted benzenes (I)*

R	μ_g^{calc}	μ_g^{expt}	μ_e^{calc}	μ_e^{expt}	λ^{calc}	f^{calc}	λ^{expt}	log ε	β_x^{calc}	β_y^{calc}	β_z^{calc}	β^{expt}
CH_3	0.52	0.38	1.09		250.1	0.04	263	2.48	0.33	0.03	0	0.18
NH_2[a]	1.68	1.53	5.69		290.5	0.15	288	3.28	3.83	0	0	0.89—1.10
NH_2[b]	1.94	1.53	3.78		273.0	0.14	288	3.28	0.54	0	2.36	0.89—1.10
NMe_2[a]	2.31	1.61	8.69		316.8	0.13	296	3.30	7.21	0	0	1.27
OH[a]	1.77	1.51	3.21		275.6	0.17	278	3.30	0.57	1.93	0	0.17
OMe[a]	1.80	1.56	3.79		278.2	0.17	271	3.33	1.01	1.60	0	
CO_2H	2.57	1.86	3.25		240.5	0.22	232	4.10	0.52	0.83	0	
CHO	3.63	2.80	5.48	7.10	246.4	0.32	241	4.20	1.10	1.43	−0.01	
CN	4.50	3.99	4.82		251.1	0.41	280	2.70	0.73	0.01	−0.05	0.48
NO_2	5.48	4.20	9.72	9.0	248.8	0.31	253	3.97	1.90	0.01	0	1.11—2.20
NO	4.30	3.10	10.64	12.2	293.8	0.27	306	3.80	7.45	1.14	0	
F	1.24	1.43	0.28		254.9	0.09	266	3.08	0.85	0	0	0.44—1.06
Cl	3.17	1.75	0.75		243.0	0.18	265	2.48	0.47	0	0	0.28
CF_3	1.89	2.56	1.72		245.0	0.01	266.5	2.58	0.29	0.05	0	

[a] Trigonal sp^2 heteroatom. [b] Tetrahedral sp^3 heteroatom.

* μ_g^{calc} and μ_e^{calc} are the calculated ground- and excited-state dipole moments (D); μ_g^{expt} and μ_e^{expt} are the corresponding experimental values;[11] λ^{calc} and λ^{expt} are the calculated and experimental[12] lowest energy transition (nm); *f* is the calculated oscillator strength; log ε is the experimental extinction coefficient;[12] β^{calc} and β^{expt} are the calculated and experimental[1] hyperpolarisabilities (in 10^{-30} cm^5 e.s.u.$^{-1}$) at an applied frequency of 1.17 eV.

calculated and published charges at the STO-3G levels but a considerable difference is observed between these and the 3-21G results with the latter showing much larger charge separation between donor and acceptor groups.

More importantly, the corresponding ground-state π-charge distributions, however, from which the hyperpolarisability is derived in part show considerable differences between the CNDOVSB and published STO-3G values, especially for electron-withdrawing groups (Table 3), and both the CHO and NO groups appear to be overestimated by a factor of 2—4 at the semiempirical level. Because these results are crucial to any scale of substituent effects, the corresponding π-charge distribution has been examined also at the more accurate 3-21G level. The results obtained show few changes in the π-charge distribution for $+M$ groups from the STO-3G method though the charge separation increases and is more comparable now to the CNDOVSB results. However, there is a marked difference between the STO-3G and 3-21G results for $-M$ groups and the latter shows a better correlation with the semiempirical results. It follows that the excited-state charges at the semiempirical level (shown in Table 3) are also probably reliable. The results show in all cases there is an increase in the magnitude of the charge at the substituent on excitation, and in nitrosobenzene a considerable movement of charge occurs from the aromatic ring to both the nitrogen and oxygen atoms as illustrated (Figure). Thus the strength of both $+M$ and $-M$ groups are enhanced relative to the ground state.

The calculated hyperpolarisabilities, however (Table 1), are derived from 50 excited states, and an analysis of the full data generated shows that the first five states contribute significantly to the final value as shown (Table 4) for phenol and nitrobenzene. In order to assess the influence of the substituent on the π-electron density of the aromatic ring for the first five excited states, therefore, a charge parameter, Q_n, has been derived by means of equation (4) where q_e is the charge at the aromatic

$$Q_n = \sum_{n}^{n'} q_e \times \frac{f_e}{f_t} \tag{4}$$

ring for a given excited state, f_e is the oscillator strength for that state, and f_t is the sum of the oscillator strengths for all the excited states considered which is restricted to run over those with values >0.1. The calculations show for a given substituent that the π-electron charge at the aromatic ring generally retains the same sign for all the excited states considered. Thus, the amino group of aniline is a donor in all the significant states considered, giving rise to aromatic ring charges of −0.4421 (*n*

Table 2. Calculated total ground- and excited-state charges[a] at the aromatic ring for monosubstituted benzenes (**I**)

R	STO-3G[b]	STO-3G	3-21G	CNDOVSB	
	q_g	q_g	q_g	q_g	q_e
H	−0.063				
CH_3	−0.015	−0.0147	−0.0633	−0.0138	−0.0385
CF_3	+0.032	+0.0326	−0.0397	+0.0053	−0.0002
NH_2[c]	+0.045	+0.0470	+0.2420	+0.0166	−0.1707
NH_2[d]	+0.039	+0.0460	+0.2766	+0.0014	−0.2858
NMe_2		+0.0342	+0.3367	+0.0214	−0.4193
OH	+0.083	+0.0830	+0.3489	+0.0352	−0.1207
OMe	+0.087	+0.0808	+0.3659	+0.0155	−0.1787
CO_2H	+0.063	+0.0623	−0.0071	+0.0564	+0.1237
CHO	+0.031	+0.0321	−0.0739	+0.0618	+0.2076
CN	+0.126	+0.1238	+0.1709	+0.1325	+0.1547
NO_2[e]	+0.258	+0.2348	+0.5466	+0.1706	+0.3701
NO_2[f]		+0.2454	+0.5891	+0.1863	+0.3133
NO	+0.147	+0.1688	+0.4720	+0.2102	+0.5410
F	+0.135	+0.1328	+0.4047	+0.1898	+0.1356
Cl		+0.1278	−0.1951	+0.2586	+0.0809

[a] q_g and q_e are the total atomic charges in the ground and first major excited state. [b] From ref. 13. [c] Tetrahedral sp^3 nitrogen. [d] Trigonal sp^2 nitrogen. [e] Standard structure (see text). [f] Geometry of NO_2 taken from representative nitroarenes (see text).

Table 4. Effect of the number of included states (*n*) on the calculated hyperpolarisabilities (β_x) of phenol and nitrobenzene at 1.17 eV

n	Phenol	Nitrobenzene[a]
1	0.0640	0.0000
2	0.2824	0.0021
3	0.7238	0.0449
4	0.6607	1.8119
5	0.6985	1.7902
25	0.5250	1.8949
50	0.5757	1.7139

[a] Standard structure with Ar–NO_2 1.40 Å.

Table 3. Calculated ground- and excited-state π-charges at the aromatic ring for monosubstituted benzenes (**I**)

R	STO-3G[b]	STO-3G	3-21G	CNDOVSB			
	q_g	q_g	q_g	q_g	q_e	n^g	Q_n
CH_3	−0.008	−0.0082	−0.0077	−0.0233	−0.0333	2	−0.0307
CF_3	+0.011	+0.0116	+0.0095	−0.0072	−0.0129	2	−0.0132
NH_2[c]	−0.095	−0.0882	−0.1052	−0.0842	−0.2863	4	−0.1306
NH_2[d]	−0.120	−0.1152	−0.1295	−0.1329	−0.4421	4	−0.2148
NMe_2	−0.134	−0.1330	−0.1415	−0.1711	−0.6559	4	−0.3569
OH	−0.102	−0.1021	−0.1073	−0.1234	−0.2868	4	−0.1527
OMe	−0.105	−0.1022	−0.1034	−0.1382	−0.3418	4	−0.1821
CO_2H	+0.034	+0.0338	+0.0592	+0.0483	+0.1328	2	+0.0681
CHO	+0.032	+0.0333	+0.0614	+0.0634	+0.2305	1	+0.2305
CN	+0.022	+0.0246	+0.0337	+0.0366	+0.0522	3	+0.0392
NO_2[e]	+0.031	+0.0290		+0.0410	+0.2555	1	+0.2555
NO_2[f]		+0.0242	+0.0531	+0.0375	+0.3133	1	+0.3133
NO	+0.037	+0.0501	+0.0926	+0.1230	+0.5776	2	+0.5590
F	−0.080	−0.0691	−0.0707	−0.0609	−0.1120	3	−0.0707
Cl		−0.0391	−0.0232	+0.0243	−0.1593	1	−0.1692

[a] q_g and q_e are π-charges in the ground and first major excited state. [b] From ref. 13. [c] Tetrahedral sp^3 nitrogen [d] Trigonal sp^2 nitrogen. [e] Standard structure (see text). [f] Geometry of NO_2 taken from representative nitroarenes (see text). [g] Number of significant excited states.

Table 5. Calculated ground- and excited-state substituent constants for monosubstituted benzenes (I)

	Experimental σ_R° values		Calculated σ_R° values		
R	Reactivity[a]	^{19}F N.m.r.[b]	Ground state	First excited state	Five excited states
CH_3	−0.10	−0.15	−0.0816	−0.1166	−0.1075
CF_3	+0.08	+0.10	−0.0252	−0.0452	−0.0462
NH_2	−0.48	−0.48	−0.4652	−1.5474	−0.7518
NMe_2	−0.52	−0.54	−0.5989	−2.2957	−1.2492
OH	−0.40	−0.43	−0.4319	−1.0038	−0.5345
OMe	−0.41	−0.43	−0.4837	−1.1963	−0.6374
F	−0.35	−0.32	−0.2132	−0.3920	−0.2475
Cl	−0.20	−0.18	+0.0851	−0.5576	−0.5922
CO_2H		+0.21	+0.1691	+0.4648	+0.2384
CHO		+0.27	+0.2219	+0.8067	+0.8068
CN	+0.10	+0.21	+0.1281	+0.1827	+0.1372
NO_2[c]	+0.16	+0.19	+0.1435	+0.8943	+0.8943
NO_2[d]	+0.16	+0.19	+0.1313	+1.0966	+1.0966
NO		+0.33	+0.4305	+2.0216	+1.9565

[a] Ref. 14. [b] Ref 15. [c] Standard structure (see text). [d] Geometry of NO_2 taken from representative nitroarenes (see text).

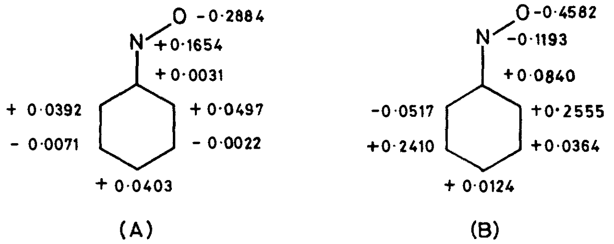

Figure. Calculated ground-state (A) and first major excited-state (B) π-electron charges for nitrosobenzene

1), −0.3988 (*n* 2), −0.1467 (*n* 3), and −0.1067 (*n* 4), whereas the nitroso group is an acceptor producing ring charges of +0.5776 (*n* 2), and +0.5470 (*n* 3). An overall ranking of substituents in terms of a substituent constant has been derived using expression (5).

$$\sigma_R^\circ(\text{calc}) = 3.5 \sum^{n} q \qquad (5)$$

A comparison of the theoretical ground-state results with those determined experimentally either using reactivity criteria[14] or ^{19}F n.m.r. studies[15] shows that a reasonable correlation is obtained from most substituents though the effect of electron-attracting groups appear to be somewhat underestimated. Considerable enhancement of the theoretical σ_R° values occurs on excitation for most substituents with the notable exception of the CN group which shows only a modest enhancement (Table 5). The results show that: (1) $NMe_2 > NH_2 > OMe > OH$ for electron donors and (2) $NO > NO_2 > CHO > CO_2H > CN$ for electron attractors.

Acknowledgements

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