

Non-linear Optical Properties of Organic Molecules. Part 4.† Calculations of the Hyperpolarisability of Sulphur-containing Systems

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A parameterisation scheme has been developed for calculating the hyperpolarisability of sulphur compounds based on correlations between computed and experimental dipole moments on the one hand and the lowest energy electronic transitions on the other. The results show that sulphur behaves both as a powerful electron donor when attached to the end of a conjugated system and also is an effective transmitter of charge when part of the conjugation path itself. A good correlation is obtained between the calculated and experimental hyperpolarisabilities of two sulphur-containing molecules.

Recent calculations of the molecular hyperpolarisability (β_{ijk}) using the sum-over-states CNDO-based methods have shown good correlations with experimental data generated by Electric Field Induced Second Harmonic Generation in solution (EFISH) for a variety of molecules containing first-row elements from H to F.¹ However, no theoretical studies have been reported on systems containing second-row elements such as sulphur and the present studies have been designed to remedy this deficiency by developing a parameterisation scheme for the element which attempts to seek the best correlation between the calculated and experimental ground-state dipole moments on the one hand and the lowest energy electronic transitions on the other as the essential criteria for a series of 20 representative molecules. We have adopted a similar procedure to that for first-row elements² by adjusting the values of the off-diagonal terms of the core Hamiltonian (H_{ij}) with a spectroscopic constant (K), the repulsion integrals (Γ_{ij}) with a screening constant (C), and additionally varying the value of the bonding parameter for sulphur $\beta(S)$ from its CNDO/S value of -18.15 eV. All calculations reported here were carried out with the CNDO/SB method which involves an initial configuration interaction treatment of ground (g) and excited state (n and n') wave functions and then evaluation of the hyperpolarisability tensor from the improved wavefunctions using the expression (1)³

$$\beta_{ijk}^{2\omega} + \beta_{ikj}^{2\omega} = (-e^3/4\hbar^2) \times \sum_{n'n} \left\{ (r_{gn}^j r_{n'n}^i r_{n'n}^k r_{ng}^k + r_{gn}^k r_{n'n}^i r_{n'n}^j r_{ng}^j) \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right] \right. \\ \left. + (r_{gn}^i r_{n'n}^j r_{n'n}^k r_{ng}^k + r_{gn}^i r_{n'n}^k r_{n'n}^j r_{ng}^j) \left[\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right] + \right. \\ \left. (r_{gn}^j r_{n'n}^k r_{n'n}^i r_{ng}^i + r_{gn}^k r_{n'n}^j r_{n'n}^i r_{ng}^i) \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right] \right\} \quad (1)$$

where $r_{gn}^i = \langle g|r^i|n \rangle$, $r_{nn}^i = \langle n'|r^i|n \rangle$, ω_{ng} is the eigen value 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 dipole moment axis.

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

The calculations were carried out on structures which were in part derived from the CSSR database.⁴ In some cases, the

crystal structures are distorted by hydrogen-bonding effects between adjacent molecules within the crystal. Because the parametrisation described is designed to calculate the molecular hyperpolarisability, β_x , the distorted crystal structures were modified by rotation of substituent groups using molecular graphics to generate essentially planar structures. In cases where no structural data were available, such as 3-amino-7-nitrodibenzothiophene, substituent groups were added directly to the crystal structure of the parent heterocycle again using molecular graphics.

On the whole the correlations between the calculated and experimental dipole moments and transition energies for a range of K , C , and $\beta(S)$ values are generally unsatisfactory and almost certainly reflect the total neglect at the CNDO/2 level of interactions between valence-shell electrons and those in the fully occupied $2s$ and $2p$ orbitals of sulphur. The best overall correlation was obtained using 80 configurations for the CI calculation with K 0.65, C 9.0, and $\beta(S) -24.0$ eV. The molecules studied are shown in Table 1 and the calculated ground-state and excited-state properties are compared with the experimental data in Table 2.

The results (with the calculated β_x value expressed throughout in units of 10^{-30} cm⁵ e.s.u.⁻¹) are generally reasonable for molecules which contain attached sulphur atoms or groups but

unsatisfactory for small heterocyclic systems containing sulphur. Thus, the agreement between the calculated and experimental transition energies is satisfactory for phenyl thiocyanates (II) and (III), and thioanisole (XVIII), and disulphides (VIII) and (IX), and the sulphide (X) but poor for thiophenes (VI) and (VII). The sulphur atom attached to a benzene ring behaves as a donor group with little evidence of back-donation from the ring into the vacant $3d$ orbitals. For example, the introduction of a nitro group (XIX) into thioanisole (XVIII) results in a hyperpolarisability which is considerably larger than that found from the insertion of an amino group (XX) (24.61 versus 5.27).

† Part 3, preceding paper.

Table 1. Structural data and calculated hyperpolarisabilities of sulphur-containing molecules *

No.	Compound	CSSR ⁴ templates	Structural type	Calculated $\omega 0$	β_x values $\omega 1.17$
(I)	Phenyl thiocyanate		A	2.32	5.81
(II)	4-Dimethylaminophenyl thiocyanate	1 304	D	10.4	16.6
(III)	4-Nitrophenyl thiocyanate	1 304	D	2.47	2.93
(IV)	2-Mercaptobenzothiazole	19 117	B	3.29	5.93
(V)	Thioindigo	32 883	B,F	0.06	2.65
(VI)	2-Mercaptothiophene	1 182, 1 215, 21 430	E	5.77	19.1
(VII)	Thiophene-2-carbaldehyde	21 430	E	1.53	2.65
(VIII)	Bis-(4-nitrophenyl) disulphide	15 643	B	4.57	9.45
(IX)	Bis-(2-aminophenyl) disulphide	6 827	B	3.49	5.19
(X)	4-Dimethylaminophenyl 4-nitrophenyl sulphide	1 507	B	13.8	32.9
(XI)	4-Nitrodiphenyl sulphide	17 825	B	9.77	24.0
(XII)	4-Dimethylaminodiphenyl sulphide	12 774	B	10.1	18.7
(XIII)	Dibenzothiophene	7 047	B	1.88	5.64
(XIV)	3-Amino-7-nitrodibenzothiophene	7 047	D	16.0	32.7
(XV)	Dibenzothiophene dioxide	7 025	B	1.06	1.42
(XVI)	3-Amino-7-nitrodibenzothiophene dioxide	7 025	D	13.1	27.0
(XVII)	4-Nitro-4'-aminodiphenyl sulphone	6 885	D	12.6	24.7
(XVIII)	Thioanisole		A	3.74	8.67
(XIX)	4-Nitrothioanisole		A	9.79	24.6
(XX)	4-Aminothioanisole	1 212, 13 615	C	3.80	5.27

* The molecular geometries are based on either crystallographic data from the CSSR database (the reference number is given),⁴ with modification thought to be appropriate for molecules in solution, or based on standard structures stored in the molecular graphics system. Any modifications to the structure are specified by the following codes: A, standard structure with recommended bond lengths and angles; B, CSSR structure adopted but any non-planar hydrogen atoms attached to sp^2 centres on carbon or nitrogen replaced by planar conformations with standard bond lengths; C, for substituted benzenes which are distorted in the crystal, substituent-group geometries have been averaged for the CSSR data and the modified substituent then added to a standard benzene ring; D, CSSR structure of parent hydrocarbon or heterocycle taken and substituents added using standard geometries; E, as D but geometries of substituents taken from related molecules; F, CSSR structure taken and unwanted substituents removed. β_x has been calculated both at zero frequency ($\omega 0$) and at an applied frequency of 1.17 eV and is expressed in units of 10^{-30} cm⁵ e.s.u.⁻¹.

Table 2. Calculated and experimental dipole moments and transition energies of sulphur-containing molecules *

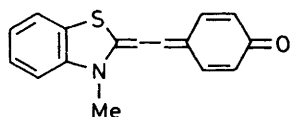
Molecule	μ^{calc}	μ^{expt}	λ^{calc}	f	λ^{expt}	log ϵ	Solvent code
(I)	4.25	3.62	328.9	0.22	270	3.13	D
(II)	6.58	5.70	339.5	0.07	310	4.41	D
			311.7	0.15			
(III)	2.79	3.10	363.3	0.03	345	2.74	D
(IV)	5.02	4.03	382.1	0.24	329	4.41	E
					320	4.43	G
(V)	0.00	0.00	527.5	0.33	545	4.28	B
(VI)	2.06	1.47	395.5	0.22	273	3.58	F
(VII)	5.55	3.55	343.0	0.16	278	3.84	D
					285	3.85	A
(VIII)	3.06	3.78	358.3	0.36	315	4.33	A
(IX)	1.30	2.30	351.5	0.03	342	3.78	A
			348.6	0.26			
(X)	8.52	6.21	366.2	0.49	330	4.1	D
(XI)	5.64	4.26	352.7	0.41	340	4.0	C
					325	4.2	C
(XII)	5.53	3.35	335.1	0.05	305	3.70	C
(XIII)	2.36	0.83	344.4	0.17	323	3.43	G
(XIV)	8.65		353.5	0.11	417	4.03	A
(XV)	4.86		316.3	0.14	318	3.23	G
(XVI)	9.55		358.0	0.27	417	4.03	A
(XVII)	7.87		330.6	0.74	338	3.82	A
(XVIII)	2.77		322.1	0.28	275		F
(XIX)	4.41		349.1	0.41	340	4.10	A
(XX)	5.00	2.58	338.1	0.04	296	3.14	C
			298.9	0.10			

* μ^{calc} and μ^{expt} are the calculated and experimental⁶ ground-state dipole moments (D), λ^{calc} and λ^{expt} are the calculated and experimental⁷ transition energies (nm), and f is the oscillator strength. In the case of molecule (1), no experimental λ value is available and the value for the 7,7-dimethyl derivative has been substituted. The solvents used for spectroscopic measurements are coded as follows: A, ethanol; B, chlorobenzene; C, no solvent given; D, hexane; E, chloroform; F, heptane; G, methanol.

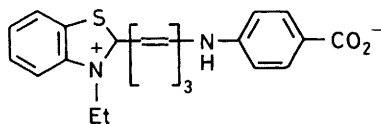
A similar effect is observed in the non-planar 4-nitro- and 4-dimethylamino-diphenyl sulphides (XI) and (XII) though less pronounced. The position is more complicated with planar phenyl thiocyanates where the 4-amino derivative (II) has a value which is considerably greater than the 4-nitro derivative (III) (16.6 versus 2.93). This apparent contradiction arises because the cyano group of the thiocyanate substituent behaves as the electron-acceptor group and the hyperpolarisability is enhanced by through donation from the dimethyl amino group in the first case and counteracted by the electron-attracting nitro group in the second with the sulphur atom acting as part of the conjugation path. A similar conjugation role for sulphur is observed in dibenzothiophene (XIII) whose low hyperpolarisability is greatly enhanced by the presence of both an electron attractor and donor at opposite ends of the molecule (XIV). The corresponding sulphones (XV) and (XVI), however, have reduced β_x values indicating that the SO₂ group is less useful either as acceptor or as part of the conjugation path.

Overall, the results suggest that the sulphur atom present in a conjugation path between donor and acceptor groups is easily polarised and transmits charge across a given molecular system as readily as the delocalised π -electrons of carbon though its effect is reduced in many cases by the non-planarity of the system in question, e.g. 4-dimethylaminophenyl 4-nitrophenyl sulphide (X). Sulphur is clearly a powerful electron donor as evidenced by its effect in 4-nitrothioanisole which has a greater calculated hyperpolarisability than 4-nitroaniline (12.2).² Indeed, the methylthio group has a comparable effect to the dimethylamino group as shown by the calculated β_x value of 25.85 for *NN*-dimethyl-4-nitroaniline.⁵ Furthermore, the absorption maximum of the former (335 nm) is considerably hypsochromic relative to the latter (388 nm) which is clearly advantageous for applications in second harmonic generation since the absorption is now well removed from the frequency-doubled 530 nm emission from an Nd:YAG laser.

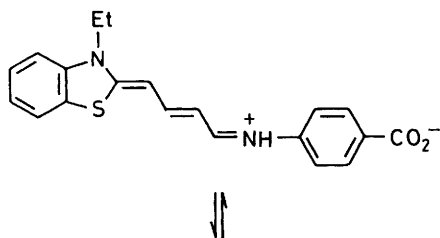
Although few studies have been reported on systems con-



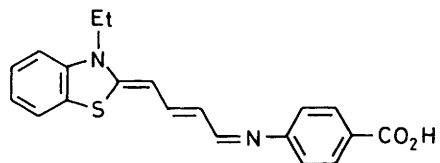
(XXI)



(XXII)



(XXIII)



(XXIV)

taining sulphur, the experimental product $\mu\beta_x$ has been reported for 4-[3-methyl-2(3*H*)-benzothiazolylidene-ethylidene]cyclohexa-2,5-dienone (XXI) and for the benzoate (XXII).⁸

Both molecules were calculated, therefore, to check the parameterisation scheme developed in the current work. Each molecule was constructed using molecular graphics from appropriate templates and calculated at the same frequency (0.656 eV) as that used for the experimental measurements.

Because the calculated ground-state dipole moments (μ) of a large number of representative molecules are known to be overestimated at the CNDOVSB level (a consequence of the original parameterisation scheme), the experimental β_x value shown in Table 3 has been derived for (XXI) and (XXII) from the product $\mu\beta_x$ by scaling the calculated μ value. The calculated results for the merocyanine (XXI) are satisfactory and both the electronic transition energy and β_x value fully reflect the experimental data in dimethyl sulphoxide (Table 3). The corresponding results for molecule (XXII) appear to be highly inaccurate and this suggests that the parameterisation scheme for sulphur is unreliable. Alternatively, however, the possibility

Table 3. Calculated and experimental results for the merocyanines^a

Molecule	λ^{expt}	λ^{calc}	β_x^{calc}	β_x^{expt}	μ^{calc}
(XXI)	560	523	54.45	39.68	12.24
(XXII)	498	690	35.66	12.69	56.09
(XXIV)	498	540	196.85	118.82	10.16

^a See Table 2 for definitions.

that structure (XXII), which may also be written as (XXIII), exists in a more stable tautomeric form (XXIV) cannot be discounted.

In simpler molecules such as 4-aminobenzoic acid, there is little doubt on the basis of dipole moment measurements⁶ that zwitterionic forms are not present in any significant concentrations either in benzene (μ 3.10 D) or dioxane (μ 3.54 D), and it seems unlikely that the charge-separated structure (XXII) could be stabilised even by the highly polar solvent dimethyl sulphoxide. Consequently, the neutral structure (XXIV) was constructed and calculated as before. The results obtained in this case show a good correlation both between the calculated and experimental transition energies and β_x values which suggests that the published structure is incorrect. It is concluded that the parameterisation adopted for sulphur is satisfactory for most systems though small heterocyclic systems are not well reproduced.

Acknowledgements

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References

- 1 J. O. Morley and D. Pugh in 'Nonlinear Optical Properties of Organic Molecules and Crystals,' eds. D. S. Chemla and J. Zyss, Academic Press, New York, 1987.
- 2 V. J. Docherty, D. Pugh, and J. O. Morley, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1179.
- 3 J. Ward, *Rev. Mod. Phys.*, 1965, **37**, 1.
- 4 Crystal Structure Search Retrieval, S.E.R.C. Daresby Laboratory.
- 5 J. O. Morley, unpublished results.
- 6 A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963, vol. I; Rahara Enterprises, San Francisco, 1974, vol. II.
- 7 J. B. Phillips, L. D. Freedman, and J. C. Craig, 'Organic Electronic Spectral Data,' Interscience, New York, 1963, vols. I-VI.
- 8 A. Dulcic, *Chem. Phys.*, 1979, **37**, 57.

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