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CHARGE DISTRIBUTIONS IN CARBONYL AND THIOCARBONYL COMPOUNDS

LCAO CALCULATIONS WITH THE ω-TECHNIQUE

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Abstract—It has been shown that the experimentally demonstrated tendency of the thiocarbonyl group to give a stronger mesomeric interaction than the carbonyl group with electron donating heteroatoms can be reproduced by a simple LCAO—MO method. A necessary condition is that the parameters reflect both the electron attracting power of the thiocarbonyl group and the small tendency for π-bond formation of second-row elements. The differences between the dipole moments of a series of conjugated carbonyl compounds and those of the thiocarbonyl analogues have been calculated and shown to be in qualitative agreement with literature values.

MOLECULAR orbital calculations on organic molecules in which heteroatoms are present are necessarily of a crude nature. Consequently emphasis in this field of study seldom is on correct numerical agreement with experiment but rather on compatibility of a chosen model with as many observed properties as possible. For this kind of problem simple LCAO procedures are well suited, and have been frequently applied in the subject now under study, namely compounds containing carbonyl and thiocarbonyl groups in various surroundings (yielding ketones, esters, chlorides, amides and their sulphur analogues). Of primary importance in this technique are the values, chosen for the parameters, since they determine the outcome and therefore represent the essentials of the model conceived. It is general custom to define Coulomb and resonance integrals for a heteroatom in terms of those for the carbon atom by (1) and (2)

$$\alpha_X = \alpha_C + h_X\beta_{CC} \tag{1}$$

$$\beta_{CX} = k_X\beta_{CC} \tag{2}$$

The values of h_X and k_X can be estimated in two ways: (a) from theoretical or physical quantities such as electronegativities, ionization potentials, bond lengths or overlap integrals, or (b) intuitively, after which they can be adapted to give reasonable agreement with experiment. Obviously the latter method is justified only if a sufficient number of results are correlated. From earlier studies on thiocarbonyl compounds it was found that the first method does not lead to satisfactory parameters. Electronegativities, for example, would make α_S equal to α_C, thus giving a non-polar C—S or C=S bond, contrary to experience. Ionization potentials are not very suited either, since they are sometimes influenced more strongly by methyl substituents than by a major change in the π electron system.[1]

The estimation of k from overlap integrals or bond strengths would make $\beta_{C=S}$ nearly equal to $\beta_{C=N}$ or $\beta_{C=O}$, which in turn would lead to a strong tendency for the

[1a] A. D. Walsh, *Trans. Faraday Soc.* **43**, 158 (1947); [b] F. I. Vilesov, *Dokl. Akad. Nauk SSSR* **132**, 1332 (1960); [c] F. I. Vilesov and B. L. Krubatov, *Ibid.* **140**, 1364 (1961).

electrons on the sulphur atom to become delocalized, quite contrary to general experience. Whether the "unrealistic" parameters for sulphur (and other heavier elements) are caused by the neglect of d-orbitals in the simple HMO approximations is not easily established, but at present it seems preferable to use parameters derived from a model chosen by chemical intuition. Some years ago[2,3] such a model was conceived, based on two considerations:

(1) The carbon sulphur bond—single as well as double—is decidedly polar; thus h_S has to differ from zero.

(2) Sulphur does not form double bonds as readily as first-row elements, thus k_S has to be lower than k for first-row elements.

With this model calculations were performed according to Hückel's LCAO procedure, with the extension that after each cycle new α and β values were chosen in accordance with the charges and bond orders found, until self-consistency was obtained. This technique is similar to that called the ω-technique by Streitwieser[4] with the exception that in our study also the resonance integrals are adapted, in a way reminiscent of the method devised by Wheland and Mann.[5]

The model was subsequently applied to the evaluation of transition energies of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in thiocarbonyl compounds of widely different structures.[2,3,6] The calculated values appeared to be proportional to the observed transition energies in good approximation.

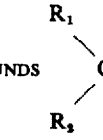
In addition, chemical properties such as the basicity of thioamides and thioureas[7] and the acidity of carboxylic acids carrying a substituent with the thiocarbonyl function[2,8] were in agreement with the model proposed in that the mesomeric electron displacement was reflected in the observed properties.

In the last paper the thiocarbonyl function was compared with the carbonyl function and it appeared—rather surprisingly—that the former was the stronger electron accepting substituent. A similar behaviour has been noticed by Lüttringhaus *et al*,[9,10] who found that the dipole moments of thiocarbonyl compounds exceed those of the corresponding carbonyl compounds if, and only if, substituents capable of strong mesomeric electron release were present in the molecule. A survey of some of the dipole data from Refs.[9,10] is shown in Table 1. More recently, Jensen[11] has pointed out that the IR spectra of thioamides indicate that the structure (Ib, X=S) has greater weight than (Ia), whereas the reverse is true for amides (X=O)

Ia Ib

[2] M. J. Janssen, *The electronic structure of organic thion compounds*. Thesis, Utrecht (1959).
[3] M. J. Janssen, *Rec. Trav. Chim.* **79**, 1066 (1960).
[4] A. Streitwieser Jr. and P. M. Nair, *Tetrahedron* **5**, 149 (1959).
[5] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).
[6] J. Sandström, *Acta Chem. Scand.* **18**, 1059 (1964), where further Refs. are found.
[7] M. J. Janssen, *Rec. Trav. Chim.* **81**, 650 (1962).
[8] M. J. Janssen, *Rec. Trav. Chim.* **82**, 931 (1963).
[9] A. Lüttringhaus and J. Grohmann, *Z. Naturforsch.* **10b**, 365 (1955).
[10] A. Lüttringhaus, R. Mecke, R. Mecke and J. Grohmann in *Elektronentheorie der Homöopolaren Bindung* p. 152. Akademie-Verlag, Berlin (1956).
[11] K. A. Jensen, *Acta Chem. Scand.* **17**, 551 (1963).

TABLE 1. DIPOLE MOMENTS (IN DEBYE UNITS) OF SOME CARBONYL AND THIOCARBONYL COMPOUNDS



(taken from Ref[9,10])

R_1	R_2	$\mu_{C=O}$	$\mu_{C=S}$	$\Delta\mu(\mu_{C=O} - \mu_{C=S})$
Cl	Cl	1·18	0·28	+0·90 (+1·46)
	$C_{10}H_{16}$ (Fenchylidene)	2·72	2·54	+0·18
	o-$C_6H_4O_2$ (catechol carbonate)	4·14	4·40	−0·26
CH_3O	CH_3O	0·87	0·90	−0·03
—S—CH_2—CH_2—S		4·46	4·86	−0·40
CH_3S	CH_3S	0·74	1·33	−0·59
$(CH_3)_2N$	CH_3	3·74	4·76	−1·02
$(CH_3)_2N$	$(CH_3)_2N$	3·37	4·70	−1·33
p-ClC_6H_4	p-ClC_6H_4	1·79	1·58	+0·21
C_6H_5	C_6H_5	3·11 (2·91)	2·88 (2·61)	+0·23 (+0·30)
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	3·90	4·44 (4·04)	−0·44 (−0·14)
p-$CH_3SC_6H_4$	p-$CH_3SC_6H_4$	3·54	3·94	−0·40
p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	5·16	6·12	−0·96

It seemed of interest to check whether the model chosen for thiocarbonyl compounds would be able to reflect the dipole moment characteristics as well. In particular it is useful to consider whether this is the result of the parameters chosen for the second row element, a Coulomb integral containing the element of electron attraction and a small resonance integral. If so, the reliability of the chosen model would be substantially strengthened.

Method of calculation. This has been described previously,[2] but a review seems warranted in the light of some new experiences. A secular equation is constructed according to the general principles of the Hückel approximation, and the resonance integrals are those appropriate to pure single and double bonds. From the π electron densities q_r and bond orders p_{rs} new parameters are constructed according to Eqs. (3) and (4).

$$\alpha_r' = \alpha_r + \omega(n_r - q_r)\beta_{CC} \tag{3}$$

$$\beta_{rs}' = \beta_{rs}(1 + 0{\cdot}5p_{rs}) \tag{4}$$

In (3) n_r is the number of π electrons submitted by atom r, and ω is a disposable parameter, which has been given the value 1·4 by several authors,[4,12] whereas the value 1·0 has been used by Wheland and Mann[5] and by the present authors.[2,3,6] In (4) β_{rs} is the single bond value. The factor 0·5 stems from the observation that overlap integrals for pure double bonds tend to be about 50% larger than for the corresponding single bonds.[13] A secular equation is constructed with the new parameters, and the process is iterated until a self-consistent solution is obtained. The calculations were

[12] A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists* p. 115, J. Wiley, New York (1961).

[13] R. S. Mulliken, C. A. Rieke, B. Orloff and H. Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

performed by an electronic digital computor with one single program. It was observed that the same results were obtained when resonance integrals corresponding to single bonds were used in the first cycle, i.e. the iterative procedure tends to even out deviations which occur only once. This makes the programmation somewhat simpler. The program was built on the Jacobi method for diagonalization of the matrices, and with symmetrical systems degenerate roots were sometimes obtained, which prevented convergency (cf. Ref[4]). This could be avoided if the symmetry was destroyed by an insignificantly small addition to one of the Coulomb integrals.

Choice of parameters. Several sets of parameters were tried, which are summarized in Table 2. Those of set 1 and 2 are somewhat higher than what is now becoming

TABLE 2

	Parameter set							
Atom (h)	1	2	3	4	5	6	7	8
C	0	0	0	0	0	0	0	0
$\ddot{N}$	1·5	1·5	1·5	1·5	1·0	1·0	1·5	1·5
$\ddot{O}$	2·5	2·5	2·5	2·5	1·7	1·7	2·5	2·5
$\dot{O}$	1·0	1·0	1·0	1·0	0·7	0·7	1·0	1·0
$\ddot{S}$	1·0	1·0	1·0	1·0	0·65	0·65	1·0	1·0
$\dot{S}$	0·5	0·5	0·5	0·5	0·35	0·35	0	0
$\ddot{Cl}$	3·0	3·0	3·0	3·0	2·0	2·0	3·0	3·0
Bond (k)	Single bond values							
C—C	1·0	1·0	0·75	0·75	0·75	0·75	1·0	1·0
C—N	1·2	1·2	0·8	0·8	0·8	0·8	1·2	1·2
C—O	1·2	1·2	0·8	0·8	0·8	0·8	1·2	1·2
C—S	0·6	0·6	0·4	0·4	0·4	0·4	1·2*	0·6
C—Cl	0·6	0·6	0·4	0·4	0·4	0·4	0·6	0·6
ω	1·0	1·4	1·0	1·4	1·0	1·4	1·0	1·0

* For comparability with the results from set 1, β_{CS} was given the value $0{\cdot}6\beta$ in single bonds, C—Y.

customary (Ref[12] p. 135) and in the following sets they are scaled down accordingly. Furthermore, two other sets were tried for the thiocarbonyl group, one with $\alpha_S = \alpha$ and $\beta_{CS} = 1{\cdot}2\beta$ (set 7) and one with $\alpha_S = \alpha$ and $\beta_{CS} = 0{\cdot}6\beta$ (set 8). Set 7 contains neither of the essential elements of the model under discussion whereas set 8 has the small resonance integral but not the element of electron attraction in common with the old model. The latter set has resemblances to those put forward by Owen,[14] and by Pullman and Pullman.[15]

DISCUSSION

At first a set of calculations was performed with the carbonyl and thiocarbonyl group in conjugation with one heteroatom (I) with systematically varied electron

[14] A. J. Owen, *Some thermodynamic and kinetic aspects of reactions of carbon and sulphur compound.* Thesis, University College, Swansea (1952); and private communication.

[15] B. Pullman and A. Pullman, *Rev. Mod. Phys.* **32**, 428 (1960).

donating capacity. For the carbonyl group parameter set 1 was used, and for the thiocarbonyl group sets 1, 7 and 8. A strong mesomeric electron release from the heteroatom Y requires a low h_Y value and/or a high k_Y value. The efficiency of the mesomeric interaction in the system (Ia $\leftrightarrow$ Ib) manifests itself in the polarization of the C=X group, i.e. in the π electron density on atom X, q_X, and in the lowering of

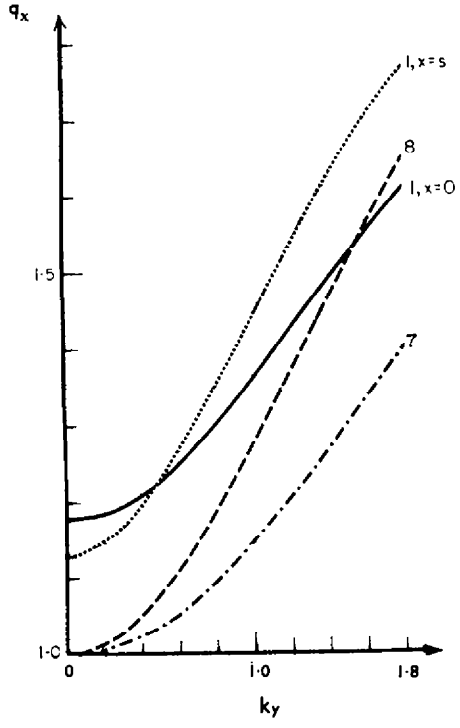


FIG. 1a. Relations between q_X and k_{CY} in the systems (I, X = O, S), $\alpha_Y = \alpha + \beta$.

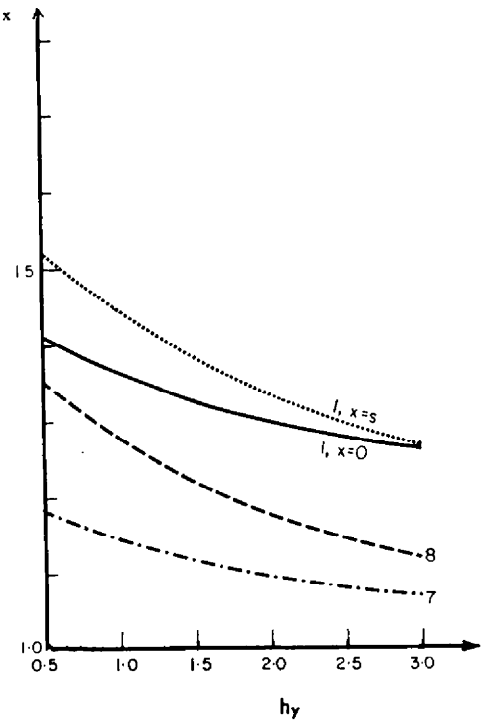


FIG. 1b. Relations between q_X and h_Y in the system (I, X = O, S), $\beta_{CY} = \beta$.

the C=X bond order p_{CX}. The variations of these quantities with h_Y and k_Y are shown in Figs. 1 and 2. It is evident that with the parameter set 1 the thiocarbonyl group responds more strongly to the electron release of Y than does the carbonyl group, as long as this release is not very weak. With parameter set 8 in all except extreme cases the thiocarbonyl group is inferior to or equal with the carbonyl group in electron attracting capacity, whereas with set 7 the thiocarbonyl group is always less polarized. It can therefore be stated with confidence that *both* an element of electron attraction *and* a low resonance integral are required for the thiocarbonyl group in the present approximation in order to bring out the general polarization characteristics observed.

Calculation of $\Delta\mu$ and μ values. As the dipole moment of a molecule is not a function of the polarization of only one bond but of the electronic structure of the whole molecule, attempts have also been made to calculate π electron moments of systems designed to simulate some of the compounds treated by Lüttringhaus *et al.* The systems chosen are (II-XII, X = O and S), and correlations were attempted with

the $\Delta\mu$ values (Table 1). The experimental dipole moments are regarded as superpositions of components due to the distribution of the delocalized electrons, π moments (μ_π), and components due to the σ electrons and the lone pairs not involved in the delocalization, σ moments (μ_σ). As a first approximation, these components are regarded as being independent of each other. Lüttringhaus *et al.* have chosen their compounds in such a way that in each pair the structures are the same except for the exchange of oxygen for sulphur. All systems except (VI) have an axis of symmetry in the C=X—bond, and therefore the π and σ moments are parallel. If it can be assumed

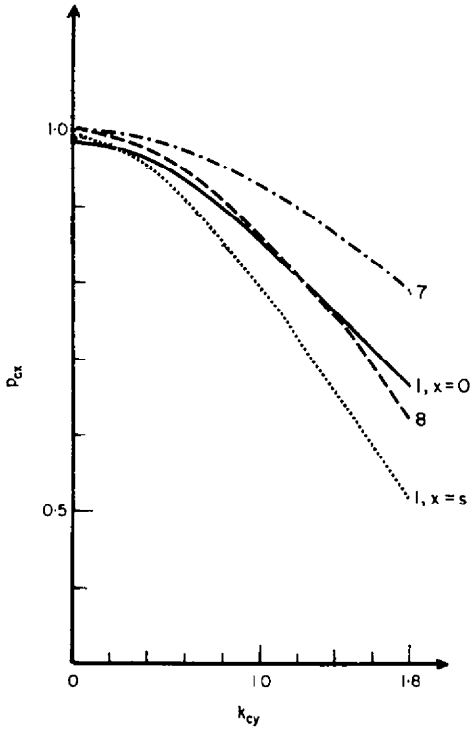


FIG. 2a. Relations between p_{CX} and k_Y in the systems (I, X = O, S), $\alpha_Y = \alpha + \beta$.

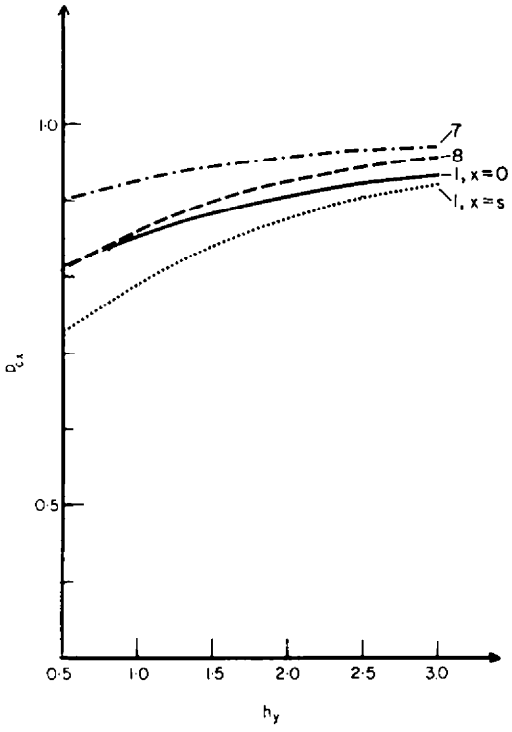


FIG. 2b. Relations between p_{CX} and h_Y in the systems (I, X = O, S), $\beta_{CY} = \beta$.

that the conformations are the same, the σ moments in a pair differ only by the difference between the contributions from the carbonyl and thiocarbonyl groups. This difference, $\Delta\mu_\sigma$, is not the same for all pairs of compounds, since the σ electrons are polarized also by the fields of more remote atoms. However, it is common practice to neglect this effect in approximate calculations of dipole moments. If this is done, it is possible, with use of the charge distributions calculated for the systems (II, X = O and S), to evaluate $\Delta\mu_\sigma$ by inserting in the expression (5) the μ values appropriate to fenchone and thiofenchone.

$$\Delta\mu = \mu_{C=O} - \mu_{C=S} = \mu_{\pi,C=O} - \mu_{\pi,C=S} + \Delta\mu_\sigma \qquad (5)$$

We thus obtain one value of $\Delta\mu_\sigma$ for each parameter set. This quantity is given in

column six of the upper division of Table 3. With use of these values and the calculated π electron distributions it is now possible to calculate $\Delta\mu$ values for each of the systems (III–XII), and for each parameter set. For the substituted benzophenone derivatives the calculations have only been performed with parameter sets 1, 5 and 8. The bond lengths and bond angles for some of the systems (II–XII) are known (for Refs see Table 3), and for the others simplified geometries have been assumed with all angles around sp^2 hybridized atoms equal to 120° and with bond lengths taken from similar molecules. The calculated μ_π and $\Delta\mu$ values are found in Table 3. There are some discrepancies between experimental and calculated $\Delta\mu$ values. The most serious deviation is shown by the phosgene–thiophosgene system, where the experimental and calculated values have different signs. (The experimental $\Delta\mu$ value may even be 1·46 D, since the direction of the thiophosgene moment is not known.) It is obvious that the simple model will always give a negative $\Delta\mu$ value, as long as only the conjugation effect is considered. However, the presence of the two strongly electronegative chlorine atoms will perturb the systems of both π and σ electrons apart from the direct action of the core fields. On the π electron system this effect might work through polarization of the σ bonds, thus increasing the electronegativity of the carbon atom. This effect is included in the framework of the Hückel method by introduction of a so called auxiliary inductive parameter, δ, which is given values between 1/10 and 1/3 (See Ref[12], p. 128ff). It is used in the expression (6) to obtain a Coulomb integral for a carbon atom

$$\alpha_C' = \alpha_C + \delta h_Y \beta_{CC} \tag{6}$$

adjacent to a more electronegative atom, Y. The parameter h_Y refers to this neighbouring heteroatom. A series of calculations was performed with the parameter sets 1, 2, 3, and 4 and with δh_Y values between 0·2 and 0·8. It appeared that the thiocarbonyl group responded more strongly to this perturbation than the carbonyl group, and for sets 3 and 4, $\Delta\mu$ values satisfactorily close to the experimental one were obtained (Fig. 3). In addition, the simplifying assumption of a constant $\Delta\mu_\sigma$ value may become particularly unrealistic in the present case. The σ electrons in the C=X bond are certainly polarized towards the carbon atom by the inductive effect of the chlorine atoms, and it is probable that the polarization is stronger for the thiocarbonyl than for the carbonyl bond. Correction for this effect will result in a more positive value for $\Delta\mu_\sigma$ than that calculated for the simple ketone–thioketone system. Thus both effects act in the right direction and probably both play a part. A similar effect is expected for other systems in which the substituents are strongly electronegative. Therefore it is significant that in the oxygen substituted compound (IV) a similar, albeit smaller deviation is found. The agreement between experimental and calculated $\Delta\mu$ values is considerably better for the benzophenone–thiobenzophenone systems than for the simpler ones, probably because the inductive effect of the atom Y is less important. Here too, however, the experimental $\Delta\mu$ values for the *p*-chloro and *p*-alkoxy derivatives are higher than the calculated ones. Thus the discrepancies are consistently explained by the operation of inductive effects, either on the σ or on the π electron system (or both). In general we can therefore conclude that with parameter sets 1–6 the $\Delta\mu$ values calculated reflect the tendency of the experimental values, i.e. a more rapid increase in polarity of the thiocarbonyl compounds than of the carbonyl compounds with increasing electron release from the substituents. The parameter sets

7 and 8 give a $\Delta\mu_\sigma$ value of −0·85 D, whereas electronegativity considerations rather point at a positive value. Furthermore, set 7 gives unrealistic $\Delta\mu$ values with all systems except (III), whereas set 8 to a certain degree can reproduce the experimental trend in the simpler systems. However, it fails completely with thiobenzophenone, for which it predicts a zero π moment, and with the *p*-chloro-, *p*-alkoxy-, *p*-alkylthio- and *p*-aminothiobenzophenones, for which positive $\Delta\mu$ values are obtained.

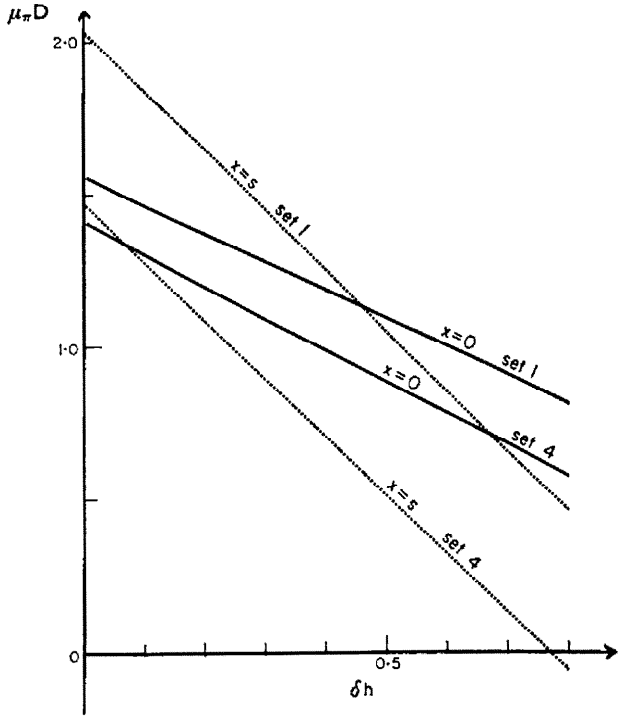


FIG. 3. Relations between μ_π and δh for phosgene and thiophosgene.

The calculated π electron distributions may be checked against the experimental dipole moments, though this is a much more hazardous undertaking than the calculation of $\Delta\mu$ values. It has previously been shown[2] that the parameter set 1 for several thiones gives π moments which are about 1·6 times too high, and therefore it is of some interest to check the other parameter sets, which ought to give reduced charge displacements. From a superficial glance at Table 3, however, it is clear that no parameter set leads to μ_π values that are smaller than those resulting from set 1 by a factor 1·6, although some sets, in particular the even numbered ones, tend to give values in the right direction. It is natural that the use of a higher ω value will damp the charge displacements, and the lower resonance integrals should work in the same direction. Parameter set 4 gives the best agreement for the aliphatic systems. For the substituted benzophenones and thiobenzophenones set 5 gives much better agreement with experiments than set 1. It is tempting to lower the k values further in order to get better agreement with experiments, but the uncertainty in current σ moments is too high to give much value to such an adjustment. At present we are satisfied to show the general effect of altering the parameters.

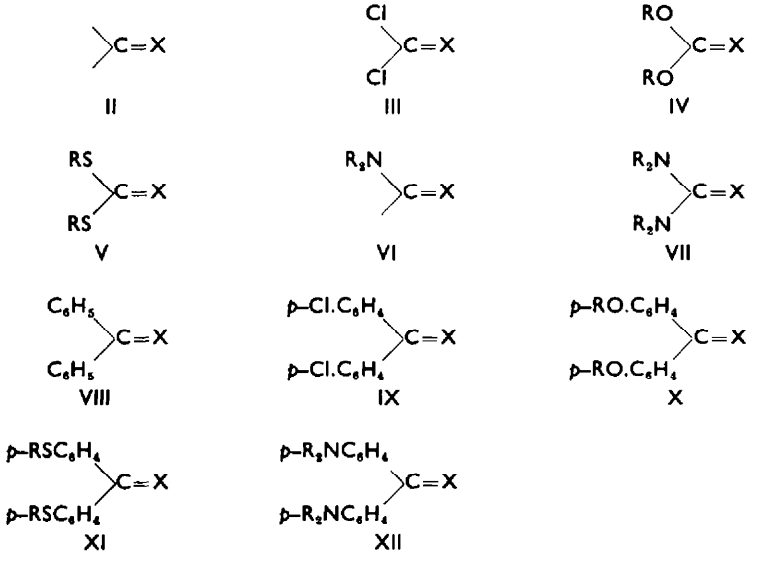
TABLE 3. CALCULATED μ_π VALUES FOR THE SYSTEMS (II—XII) AND $\Delta\mu$ VALUES FOR (II—V) AND (VII—XII) IN DEBYE UNITS. THE POSITIVE DIRECTION IS C → X

System	Parameter set	μ_π		$\Delta\mu_\pi$	$\Delta\mu_{calc}$	Ref.[a]
		X = O	X = S			
II	1	1·03	1·01	0·02	0·16[b]	
	2	0·90	0·83	0·07	0·11	
	3	1·31	1·20	0·11	0·07	
	4	1·11	0·96	0·15	0·03	
	5	0·92	0·84	0·08	0·10	
	6	0·78	0·67	0·11	0·07	
	7	1·03	0	1·03	−0·85	
	8	1·03	0	1·03	−0·85	
III	1	1·56	2·04	−0·48	−0·32	16, 17
	2	1·40	1·76	−0·36	−0·25	
	3	1·62	1·77	−0·15	−0·08	
	4	1·41	1·47	−0·06	−0·03	
	5	1·42	1·75	−0·33	−0·23	
	6	1·25	1·48	−0·23	−0·16	
	7	1·56	0·22	+1·33	+0·48	
	8	1·56	0·37	+1·18	+0·33	
IV	1	3·36	5·39	−2·03	−1·87	
	2	3·05	4·69	−1·64	−1·52	
	3	2·91	3·93	−1·02	−0·95	
	4	2·57	3·31	−0·74	−0·71	
	5	3·02	4·54	−1·52	−1·42	
	6	2·67	3·83	−1·16	−1·09	
	7	3·36	2·35	+1·01	+0·16	
	8	3·36	3·93	−0·57	−1·42	
V	1	2·52	4·04	−1·52	−1·36	
	2	2·29	3·49	−1·20	−1·10	
	3	2·53	3·34	−0·81	−0·74	
	4	2·23	2·82	−0·59	−0·56	
	5	2·32	3·49	−1·17	−1·07	
	6	2·05	2·95	−0·90	−0·83	
	7	2·52	1·13	+1·39	+0·54	
	8	2·52	2·42	+0·10	−0·75	
VI	1	3·27	5·18			18, 19
	2	2·94	4·43			
	3	2·94	3·97			
	4	2·58	3·32			
	5	2·94	4·35			
	6	2·58	3·62			
	7	3·27	2·04			
	8	3·27	3·60			
VII	1	4·35	7·04	−2·69	−2·53	20, 21
	2	3·96	6·19	−2·23	−2·12	
	3	3·90	5·52	−1·62	−1·55	
	4	3·45	4·67	−1·22	−1·19	
	5	3·94	6·07	−2·13	−2·03	
	6	3·48	5·13	−1·65	−1·58	
	7	4·35	3·36	+0·99	+0·14	
	8	4·35	5·59	−1·24	−2·09	

TABLE 3 (*contd.*)

System	Parameter set	μ_π X = O	μ_π X = S	$\Delta\mu_\pi$	$\Delta\mu_{calc}$	Ref.[a]
VIII	1	2·08	2·33	−0·25	−0·09	
	2	1·86	1·97	−0·11	0	
	3	2·85	2·90	−0·05	+0·02	
	4	2·50	2·38	+0·12	+0·15	
	5	1·99	2·03	−0·04	+0·06	
	6	1·76	1·67	+0·09	+0·16	
	7	2·08	0	+2·08	+1·23	
	8	2·08	0	+2·08	+1·23	
IX	1	2·51	2·88	−0·37	−0·21	
	5	2·38	2·51	−0·13	−0·03	
	8	2·51	0·51	+2·00	+1·15	
X	1	4·31	5·19	−0·88	−0·72	
	5	3·91	4·42	−0·51	−0·41	
	8	4·31	2·62	+1·69	+0·84	
XI	1	3·46	4·17	−0·71	−0·55	
	5	3·30	3·63	−0·33	−0·23	
	8	3·46	1·59	+1·87	+1·02	
XII	1	5·81	7·11	−1·30	−1·14	
	5	5·13	5·99	−0·86	−0·76	
	8	5·81	4·29	+1·52	+0·67	

[a] Refers to structure determinations
[b] for system II, $\Delta\mu_\sigma$



Systems found in Table 3.

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