Theoret. chim. Acta (Berl.) 6, 333—340 (1966)

Self-Consistent Perturbation Theory for Conjugated Molecules

III. Values of the Inductive Parameters for Aza and Methyl Substitution Derived from ESR Data

A. T. Amos

Department of Mathematics, University of Nottingham, England

Received August 5, 1966

Using self-consistent perturbation theory the first order changes in the spin densities of positive and negative ions of substituted hydrocarbons are calculated. By comparison with ESR hyperfine splitting constants the values of the inductive parameters for aza and methyl substitution are obtained. For aza substitution the most reliable estimate is -1.73 eV in agreement with the best theoretical estimate of -1.85 eV. For methyl substitution in anthracene the data can best be explained by using different values for the positive and negative ions so as to allow for hyperconjugation. The values obtained are $-0.3\,\beta$ for the positive ion and $-0.15\,\beta$ for the negative ion. The theoretical values are $-0.33\,\beta$ and $-0.11\,\beta$.

Mittels selbstkonsistenter Störungsrechnung wurden die Spindichteänderungen erster Ordnung von substituierten Kohlenwasserstoffen berechnet. Durch Vergleich mit ESR-Hyperfeinstrukturkonstanten erhält man dann die induktiven Parameter für Aza- und Methylsubstitution. Für Azasubstitution ist der wahrscheinlichste Wert $-1{,}73$ eV, in guter Übereinstimmung mit dem als dem besten geltenden Wert von $-1{,}85$ eV. Bei Methylsubstitution im Anthrazen benötigt man für positive und negative Ionen verschiedene Werte, um die Hyperkonjugation zu berücksichtigen, und zwar $-0{,}3\,\beta$ für das positive Ion und $-0{,}15\,\beta$ für das negative. Theoretische Werte sind $-0{,}33\,\beta$ bzw. $-0{,}11\,\beta$.

La théorie des perturbations self-consistantes est utilisée pour le calcul de la variation du premier ordre des densités de spin des ions positifs et négatifs des hydrocarbures substitués. Les valeurs des paramètres inductifs pour les dérivés aza ou méthylés sont obtenues par comparaison avec les constantes de séparation hyperfine en R.P.E. Pour une substitution aza l'estimation la plus sûre donne $-1{,}73$ eV en accord avec la meilleure valeur théorique de $-1{,}85$ eV. Pour la substitution du méthyle dans l'anthracène les données expérimentales sont le mieux expliquées en utilisant des valeurs différentes pour les ions positifs et négatifs afin de tenir compte de l'hyperconjugaison. Les valeurs obtenues sont $-0{,}3\,\beta$ pour l'ion positif et $-0{,}15\,\beta$ pour l'ion négatif. Les valeurs théoriques sont $-0{,}33\,\beta$ et $-0{,}11\,\beta$.

1. Introduction

In their 1962 paper on nitrogen heterocyclics Carrington and Santos-Veiga [5] were able to give a theoretical explanation of the ESR spectra they had obtained for several aza substituted hydrocarbons. There are many fruitful ideas implicit in their treatment and one of these, which was also used by Bolton, Carrington and McLachlan [4] to discuss methyl substitution in anthracene, is the basis of this note.

It will be recalled that the theoretical treatment of ESR proton hyperfine splittings in hydrocarbons rests on the McConnell relation [*12*]:

$$a_H = -Q\varrho \tag{1}$$

which states that the hyperfine splitting constant a_H is proportional to the unpaired spin density ϱ at the attatched carbon atom. The same relation holds for proton splittings in the substituted hydrocarbon:

$$a^s_H = -Q\varrho^s . \tag{2}$$

One might hope to use (2) to find values for the parameters needed to describe substitution in hydrocarbons by choosing those values which give the spin densities ϱ^s in best agreement with the a^s_H. Unfortunately, this approach is not satisfactory since the McConnell relation is not sufficiently accurate. CARRINGTON and SANTOS-VEIGA noticed that if (1) and (2) were combined then the ratios a^s_H/a_H and ϱ^s/ϱ should be equal and this turns out to be a much more satisfactory method for comparing theory and experiment since many of the discrepancies involved in (1) and (2) are removed. Indeed when the Hückel method is used to calculate the spin densities then quite good agreement between the theoretical and experimental ratios is found for nitrogen heterocyclics [*5*] and excellent agreement for methyl substitution [*4*].

A possible objection to this is the use of Hückel spin densities since the Hückel method is known to be unreliable especially for heterocyclics where there is non-uniform charge distribution. One purpose of this note is to remove this objection by using the S.C.F. method to compute the ϱ^s. The main purpose, however, is to find satisfactory values for the inductive parameters necessary to describe aza and methyl substitution. To do this we have used the S.C.F. perturbation theory [*1*] described in paper I to expand ϱ^s as a power series in the inductive parameter treated as the perturbation parameter. We then take the view that, to be acceptable, the value of this parameter must be such as to lead to agreement between the ratios a^s_H/a_H and ϱ^s/ϱ. Both for aza and methyl substitution this points unmistakably to values in agreement with theoretical estimates.

2. Theory

There are several methods available for computing the spin density distribution for conjugated hydrocarbon ions [*8*]. The simplest is to assume that in the ion the unpaired electron occupies the lowest unoccupied (negative ion) or highest occupied (positive ion) orbital of the ground state. Writing this orbital as a linear combination of atomic orbitals:

$$\psi = \sum_r c^0_r \omega_r \tag{3}$$

where the zero is to indicate ψ is for the hydrocarbon, then the spin density at the rth carbon will be

$$\varrho^0 = (c^0_r)^2 . \tag{4}$$

Eq. (4) does not always give very good results since correlation between electrons with different spins is not allowed for. This can be remedied to some extent by using the self-consistent version [*8*, *17*] of McLACHLAN's approximate unrestricted Hartree-Fock method [*14*]. The spin density will then be

$$\varrho^M = \varrho^0 + \tfrac{1}{2} \sum_s (c_s^0)^2 \pi_{rs} \tag{5}$$

where π_{rs} are the S.C.F. atom-atom polarizabilities in units of β (-4.78 eV). The ϱ^M are approximations to the correct unrestricted Hartree-Fock spin densities which have been computed by Snyder and Amos [*17*] for a large number of hydrocarbon ions.

The inductive effect of a hetero-atom or group substituted into a hydrocarbon can be expressed by changing the one-electron terms in the Hamiltonian. If this change is of an amount $\lambda\beta$ at the position of substitution then it is possible to treat λ as a perturbation parameter and to find in a *self-consistent* way numerical values for first order changes in orbital coefficients and energy levels.

In particular the orbital coefficients will be given by

$$c_r^s = c_r^0 + \lambda c_r' \tag{6}$$

so that corresponding to (4) we have that

$$\varrho^s = (c_r^s)^2 = \varrho^0 + 2\lambda c_r^0\, c_r' \tag{7}$$

to first order, and the first order change in ϱ^0 is $\varrho_0' = 2c_r^0\, c_r'$. In the same way it is possible to find the first order change ϱ_M' in ϱ^M.

Using the method described in paper I of this series [*1*] we have computed the $\{c_r'\}$ for substitutions in napthalene, anthracene and diphenyl and hence have calculated the ϱ_0' and ϱ_M'. To compare theory and experiment we use the relation

$$a_H^s/a_H = \varrho^s/\varrho = 1 + \lambda\, \varrho'/\varrho \tag{8}$$

which can be simplified to

$$\lambda\, \varrho'/\varrho = (a_H^s - a_H)/a_H\,. \tag{9}$$

Relation (9) is the most useful from our point of view since if we put $R = \varrho'/\varrho$ and define

$$\varDelta = \frac{a_H^s - a_H}{a_H} \tag{10}$$

then we see that λ will be given directly by the ratio $\varDelta/R$. There are, of course, two possible choices for R depending on which of ϱ^0 and ϱ^M is taken to be the spin density.

3. Inductive Parameter for Aza Substitution

Carrington and Santos-Veiga [*5*] and Henning [*9*] have obtained the ESR spectra of a number of nitrogen heterocyclics. Using their values of the hyperfine splitting constants in these molecules and the corresponding values for the parent hydrocarbons the ratios $\varDelta$ (Eq. 10) can be found and these are given in Tab. 1. We have then computed the values of $\varDelta/R^0$, $\varDelta/R^M$, at every atom and these are also given in Tab. 1. If our theory and calculations were completely correct then all these values would be the same and would equal the value of λ for aza substitution. Clearly they are not all the same but if we exclude the six atoms marked (*) the range of values for the remaining ten atoms is not too large. For all but one of the six starred atoms the reason for the anomalous value of λ is not too difficult to understand. In all but the 4 position of 1,5 diazanaphthalene, the spin densities in both the unsubstituted and the substituted molecules are small and the values

Table 1. *Values of Δ, Δ/R^0, Δ/R^M in some nitrogen heterocyclics*

Molecule	Atom	Δ[a]	$\lambda^0 = \Delta/R^0$	$\lambda^M = \Delta/R^M$
1, 4 diazanaphthalene	2	0.819	0.498	0.384
	5	−0.514	0.406	0.395
	6	−0.207	0.252	0.310
1, 5 diazanaphthalene	2	0.606	0.809	0.425
	3*	−0.081	−1.125	1.162
	4*	0.188	2.540	1.655
9, 10 diazaanthracene	1	−0.343	0.503	0.454
	2*	−0.019	0.090	0.376
1, 4, 5, 8 tetraazaanthracene	2	0.739	0.574	0.410
	9	−0.288	0.326	0.333
γ, γ dipyridyl	2	−0.105	0.276	0.191
	3*	+0.023[b]	0.011	−0.006
	3*	−2.023[b]	—	0.535
α, α dipyridyl	3*	0.255[b]	—	0.032
	3*	−2.255[b]	—	−0.283
	4	−0.135	0.456	0.444
	5*	1.441[b]	0.373	−0.205
	5*	−3.441[b]	—	0.491
	6	−0.547	0.316	0.254
Average[c]			0.442	0.361

[a] From ref. 5 and 9.

[b] See text.

[c] Excluding the values at atoms marked *.

of ϱ' are also small. This means that the ratios R^0 and R^M are unreliable since second order effects may be important. In addition the values of the Δ may be rather unreliable. Therefore at these starred atoms we cannot expect reasonable values for the λ since our theory is not accurate enough.

In this context the 3 and 5 positions of the dipyridyls are particularly interesting. At this position the values of ϱ^0 and ϱ^M in the parent hydrocarbon differ in sign indicating that correlation effects are most important. This also means that there is uncertainty as to the sign of the a_H at this position. We have, therefore, computed two Δ values at these positions on the assumptions firstly that the coupling constants have the same sign in the diphenyl and the dipyridyls and secondly that they have opposite signs. The second assumption is, of course, only tenable when the ϱ^M and R^M are used since the ϱ^0 are always positive. The λ values do give some indication that the second assumption is correct. However, the spin densities are so small that any slight changes could lead to the opposite result. This point is well illustrated by the value of ϱ^0 at the 3 position in $\alpha\alpha$ dipyridyl. Using Eq. (7), ϱ^0 turns out to be negative and second order terms have to be included to make it positive. For this reason we have no λ^0 value at this position. In view of the importance of a correct value of the ϱ^M at positions 3 and 5 in the

Table 2. *Comparison of experimental and theoretical values of a_H (in gauss) for nitrogen heterocyclics*

Molecule	Atom	Experimental[a]	Theoretical	
		a_H	a_H^0	a_H^M
1, 4 diazanaphthalene	2	-3.33 ± 0.01	-3.16	-3.24
	5	-2.38 ± 0.01	-2.14	-2.57
	6	-1.45 ± 0.01	-1.17	-1.39
1, 5 diazanaphthalene	2	-2.95 ± 0.01	-2.44	-2.77
	3	-1.69 ± 0.01	-1.89	-1.78
	4	-5.77 ± 0.03	-4.99	-5.03
9, 10 diazaanthracene	1	-1.80 ± 0.02	-1.92	-2.01
	2	-1.54 ± 0.02	-1.42	-1.54
1, 4, 5, 8 tetraazaanthracene	2	-2.73	-2.47	-2.50
	9	-3.96	-3.40	-3.83
γ, γ dipyridyl	2	-2.37 ± 0.01	-2.21	-2.13
	3	$\pm 0.44 \pm 0.01$	-0.82	-0.16
α, α dipyridyl	3	$\pm 0.54 \pm 0.01$	—	$+1.67$
	4	-4.58 ± 0.08	-4.61	-4.71
	5	$\pm 1.05 \pm 0.03$	-1.16	-0.66
	6	-1.20 ± 0.03	-0.63	-0.59

[a] Ref. 5 and 9. The signs of the a_H are assumed to be negative except at the 3 and 5 positions of the dipyridyls where there is a possible positive a_H.

unsubstituted hydrocarbon we have taken it to be the value computed by SNYDER and AMOS [*17*] using the accurate unrestricted Hartree-Fock method.

For the reasons just given we think it reasonable to ignore the λ values at the starred atoms when finding the best average values of λ. These reasons do not, it is true, apply to the 4 position of 1,5 diazanaphthalene but the values of λ we have obtained from the ESR data at this position are so obviously anomalous that we propose to ignore them too. Using the ten remaining values we find the average values of λ^0 and λ^M are -2.11 eV and -1.73 eV respectively.

Table 3. *Spin densities at nitrogen atoms and comparison of experimental and theoretical values for a_N (in gauss)*

Molecule	Theoretical[a]				Experimental[b]
	ϱ_N^0	ϱ_N^M	a_N^0	a_N^M	a_N
1, 4 diazanaphthalene	.256	.279	5.58	5.41	5.70 ± 0.02
1, 5 diazanaphthalene	.151	.173	3.29	3.36	3.37 ± 0.02
9, 10 diazaanthracene	.228	.266	4.97	5.16	5.15 ± 0.05
1, 4, 5, 8 tetraazaanthracene	.121	.129	2.64	2.50	2.41
γ, γ dipyridyl	.140	.169	3.05	3.28	3.59 ± 0.02
α, α dipyridyl	.148	.157	3.23	3.05	2.54 ± 0.05

[a] Coupling constants computed using the relations $a_N^0 = 21.80\,\varrho_N^0$ and $a_N^M = 19.40\,\varrho_N^M$.
[b] Ref. 5 and 9.

Once the value of λ is fixed it is possible to work backwards and predict the values for a_H^s for comparison with experiment. This has been done using the averaged λ^0 and λ^M and the results are given in Tab. 2. The agreement with experiment is quite satisfactory except for the small coupling constants in the dipyridyls.

It is also possible to find the nitrogen spin densities and the ϱ_N computed in this way are given in Tab. 3. At present there is some controversy as to the correct relationship between nitrogen hyperfine splittings and spin densities [*3*, *18*]. A recent discussion [*13*] has inclined marginally to a simple linear relationship between the splitting constant and the nitrogen spin density:

$$a_N = Q_N \varrho_N \,.$$

With constant Q_N set equal to 19.40 for the ϱ_N^M and 21.80 for the ϱ_N^0 we have predicted the values of a_N using the spin densities given in Tab. 3. These predicted a_N agree reasonably well with experiment (see Tab. 3). We would not expect significantly better results if we had taken into account the spin densities on the adjacent carbon atoms.

4. Inductive Parameter for Methyl Substitution

In this section we shall attempt to find an inductive parameter for methyl substitution using the same method as was used in the previous section. The experimental results we shall use are those obtained by Bolton et al. [*4*] for the positive and negative ions of 9-methylanthracene and 9, 10 dimethylanthracene. For each atom there are two possible values of Δ, i.e. Δ^+, Δ^-, the former being obtained from the experimental data for the positive ion and the latter from the data for the negative ion. This given four sets of values for λ which may be denoted, with the obvious notation, by λ_+^0, λ_+^M, λ_-^0, λ_-^M. Only the quantities λ_+^0 and λ_-^0 have been calculated, however, since the λ^M give no extra information. The λ_-^0 and λ_+^0 are given in Tab. 4 and it is immediately obvious that the spread of values is much greater than that found for nitrogen substitution so that any conclusions drawn from Tab. 4 will be much less definite than those drawn from Tab. 1.

Table 4. *Values of Δ and Δ/R^0 for methyl substituted anthracenes*

Molecule	Atom	Positive Ion Δ^+	Negative Ion Δ^-	$\lambda_+^0 = \dfrac{\Delta^+}{R_+^0}$	$\lambda_-^0 = \dfrac{\Delta^-}{R_-^0}$
9, methylanthracene	1	−.096	.073	−.183	−.139
	2	.043	−.115	−.127	−.340
	3	−.150	.102	−.273	−.186
	4	−.084	.011	−.521	−.070
	10	.057	−.072	−.085	−.108
9, 10 methylanthracene	1	−.183	.058	−.269	−.084
	2	−.150	−.032	−.731	+.165
Average				−.312	−.155[a]

---

[a] Excluding the positive value of λ_-^0.

Table 5. *Comparison of theoretical and experimental values for a_H (in gauss) in methylanthracenes*

Molecule	Atom	Positive Ion[a]		Negative Ion[a]	
		Theory	Experiment[b]	Theory	Experiment[b]
9 methylanthracene	1	2.60	2.81	2.96	2.94
	2	1.55	1.46	1.49	1.39
	3	1.16	1.19	1.70	1.73
	4	2.95	2.85	2.80	2.77
	10	8.03	7.03	4.99	5.16
9, 10 methylanthracene	1	2.45	2.54	3.03	2.90
	2	1.31	1.19	1.62	1.52

[a] The signs of the a_H are negative.

[b] Ref. 4.

However, it is obvious that λ must be negative and excluding the positive value in the table the average is -0.24. If the separate averages of λ_+^0 and λ_-^0 are considered then a very surprising factor appears. This is the fact that the former is twice as big as the latter. We, therefore, draw the rather tentative conclusion that the inductive parameter for methyl substitution should be different in the positive and the negative ions. This conclusion is impossible to justify using a purely inductive model but Bolton et al. [*4*] have shown that this is precisely what is to be expected on the basis of hyperconjugation. Moreover, using the parameters of Coulson and Crawford [*6*] they predict that $\lambda_+ = -0.230$ and $\lambda_- = -0.131$ a ratio of 1.8:1 and these figures are quite close to those we have obtained. So our conclusion is that the inductive model can be used to describe methyl substitution provided different inductive parameters are used for different states to allow for hyperconjugation. In the case of substitution in anthracene we recommend $\lambda = -0.3$ for the positive ion, $\lambda = -0.15$ for the negative ion and for the ground state the average value $\lambda = -0.24$. For substitution in other molecules the values of λ for the positive and negative ions will change along the lines discussed in [*4*] but we expect the average value to be fairly constant.

Using the values for anthracene we have predicted the hyperfine splittings a_H for the molecules considered by Bolton et al. The theoretical results are compared with experiment in Tab. 5. The agreement is excellent for the negative ions but only fair for the positive ones.

5. Discussion

To begin with it is useful to discuss how far the inductive parameters derived in this note from ESR data agree with theoretical estimates. In paper I [*1*] it was pointed out that the inductive parameter equals $z_s + \frac{1}{2}\gamma'_{ss}$ where z_s is the change in the one electron terms and γ'_{ss} the change in the Coulomb integral at the substituent. Dewar and Gleicher [*7*] have recently considered the value of these parameters for aza substitution and find $z_s = -2.96$ eV and $\gamma'_{ss} = +1.361$ eV giving a compositive value -2.28 eV. This agrees quite well with the value of -2.11 eV for λ^0. However, Sinanoğlu and Orloff [*16*] have made a more rigorous estimate of γ'_{ss} and find a value of 2.22 eV. Combining this with the Dewar and

GLEICHER value of z_S gives -1.85 eV for the composite inductive parameter. This is in good agreement with $\lambda^M = -1.73$ eV and we would expect this to be a more reliable estimate than λ^0. Note, however, that all of these values are larger than some which have been used previously for aza substitution [*2*, *10*, *15*].

We have already referred to the values of $\lambda_+ = -0.23$, $\lambda_- = -0.13$, $\lambda_{AV} = -0.17$ obtained for methyl substitution in anthracene by BOLTON et al. [*4*]. However, their calculation used the Hückel values for the orbital energies of the molecular orbitals in anthracene. When the self-consistent values are used we obtain $\lambda_+ = -0.33$, $\lambda_- = -0.11$. Our empirical values are $\lambda_+ = -0.31$, $\lambda_- = -0.155$.

There is clearly some need to improve on some of the estimates especially those for methyl substitution. Any improvement must, however, await further experimental results. It would, in particular, be interesting to have experimental information on the positive ions of the nitrogen heterocyclics to check that the value of the aza inductive parameter is the same in the positive and negative ions. Further information on methyl substitution is needed to verify the need for different parameters in the positive and negative ions. ESR experiments on triplet states would also be of interest since the theory predicts that spin density changes in triplet states of substituted alternants are second order and therefore the hyperfine splittings should change only slightly from those of the parent hydrocarbon.

References

[*1*] AMOS, A. T., and G. G. HALL: Theoret. chim. Acta **5**, 148 (1966).
[*2*] — — Mol. Physics **4**, 25 (1961).
[*3*] ATHERTON, N. M., F. GERSON, and J. N. MURRELL: Mol. Physics **5**, 509 (1962).
[*4*] BOLTON, J. R., A. CARRINGTON, and A. D. MCLACHLAN: Mol. Physics **5**, 31 (1962).
[*5*] CARRINGTON, A., and J. DOS SANTOS-VEIGA: Mol. Physics **5**, 21 (1962).
[*6*] COULSON, C. A., and V. A. CRAWFORD: J. chem. Soc. **1953**, 2052.
[*7*] DEWAR, M. J. S., and G. J. GLEICHER: J. chem. Physics **44**, 759 (1966).
[*8*] HALL, G. G., and A. T. AMOS: Adv. in Atomic and Molecular Physics **1**, 1 (1965).
[*9*] HENNING, J. C. M.: J. chem. Physics **44**, 2139 (1966).
[*10*] HINCHLIFFE, A.: Theoret. chim. Acta **5**, 208 (1966).
[*11*] LEVY, D. H.: Mol. Physics **10**, 233 (1966).
[*12*] MCCONNELL, H. M.: J. chem. Physics **24**, 632 (1956).
[*13*] MCDOWELL, C. A., and K. F. G. PAULUS: Mol. Physics **7**, 541 (1964).
[*14*] MCLACHLAN, A. D.: Mol. Physics **2**, 271 (1959).
[*15*] MCWEENY, R., and T. E. PEACOCK: Proc. physic. Soc. **A 70**, 41 (1957).
[*16*] SINANOĞLU, O., and M. K. ORLOFF: Modern Quantum Chemistry, Vol. I, 221. New York: Academic Press 1965.
[*17*] SNYDER, L. C., and A. T. AMOS: J. chem. Physics **42**, 3670 (1965).
[*18*] STONE, E. W., and A. H. MAKI: J. chem. Physics **39**, 1635 (1963).

Dr. A. T. AMOS
Department of Mathematics
University of Nottingham
University Park
Nottingham, England