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Annotatio

Hyperconjugation and Induction in the Methyl Benzenes

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Charge distributions of methyl substituted benzenes, agreeing completely with those calculated by Flurry using an inductive model and the PPP method, can be obtained also in the Hückel scheme by a simple perturbation treatment.

In a recent article in this journal [1] R. L. Flurry has presented the numerical results of a full Pariser-Parr-Pople calculation for benzene and six different polymethyl benzenes. In Tab. 2 of this paper he gives the total π-electron charges on each of the six carbon atoms of the ring in all seven molecules. The model used in this calculation was a purely inductive one, in which the effect of a methyl group was taken to be represented by a change in the Coulomb term and the two-electron one-centre repulsion integral (γ_{11}) for each atom to which a methyl group was attached.

I wish to make three comments on the charge distribution calculated by Flurry.

1. The π-electron charges presented by Flurry are given to three decimal places. To this accuracy all the charge distributions for all the various methylbenzenes can be obtained by appropriate simple addition of the values for toluene. Flurry's values of the displaced charge (in electrons) when the methyl group is placed at position 1, are

$$\delta q_1 = -0.062, \quad \delta q_2 = \delta q_6 = +0.028, \quad \delta q_3 = \delta q_5 = -0.003, \quad \delta q_4 = +0.013. \quad (1)$$

If we now suppose that, e.g., in *m*-Xylene, with two methyl substituents, the final charge distribution is to be found by addition of two sets of values such as those in (1), but based on positions 1 and 3, we obtain for this molecule

$$\delta q_1 = \delta q_3 = -0.065, \quad \delta q_2 = +0.056, \quad \delta q_4 = \delta q_6 = +0.041, \quad \delta q_5 = -0.006.$$

This is in complete agreement (to 0.001) with the values calculated in [1]. A similar situation exists for all the other molecules. Thus, in this model, there is no need to make a full calculation of the charge distribution for each separate molecule.

This additive character had previously been found by Coulson and Crawford [2] by a much simpler and presumably less accurate Hückel type of calculation. An additive character of this kind has already been discussed by Coulson and Looyenga [3, 4] for the geometrical changes found by aza-replacements of carbon atoms in benzene.

2. Since the charge distributions are additive for each methyl substitution, so also will be the dipole moments. Flurry said that he had not calculated any of these moments. In fact there is no need to do so, since provided that toluene fits with experiment, all the other molecules will also fit.

3. The basic charge distribution in this theory is that of toluene. It is interesting to see that the δq in (1) are very close to the very simple theoretical values to be expected on first-order perturbation theory using a Hückel model, with $\delta\alpha = k\beta$ for every carbon atom to which a methyl group is attached. In terms of the atom-atom polarizabilities $\pi_{r,1}$ introduced by Coulson and Longuet-Higgins [5, 6, particularly p. 25 of Reference 6] the charges displaced in toluene should be $\delta q_r = \pi_{r,1}\,\delta\alpha$. Thus

$$\begin{aligned} \delta q_1 &= \frac{43}{108\beta}\delta\alpha = \frac{43}{108}k, & \delta q_2 &= \delta q_6 = \frac{-17}{108}k, \\ \delta q_3 &= \delta q_5 = \frac{1}{108}k, & \delta q_4 &= -\frac{11}{108}k. \end{aligned} \tag{2}$$

If we choose the inductive parameter k such that the value of δq_1 in this expression agrees with the Flurry value in (1) (i.e. put $k = -0.156$), we predict

$$\delta q_1 = -0.062,\ \delta q_2 = \delta q_6 = 0.025,\ \delta q_3 = \delta q_5 = -0.001,\ \delta q_4 = 0.025. \tag{3}$$

The values in (3) agree very closely with those in (1), and show precisely the same alternating character round the ring. It is very satisfactory that the very simple treatment by atom-atom polarizabilities in the Hückel scheme should agree so well with the much more elaborate many-electron treatment by the P.P.P. method. But this agreement does not in itself imply that either model is a complete description of hyperconjugation.

References

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