

Short communication

ON THE DIPOLE MOMENTS OF FLUOROBENZENES BY QUANTUM CHEMICAL METHODS

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In a recent paper Doraiswamy and Sharma [1] reported the dipole moments of fluorobenzenes calculated by CNDO/2 and INDO methods using two different sets of geometry parameters: the first corresponds to the standard values of Pople and Beveridge [2], the second is regarded as r_0 structure obtained by fitting the geometries to reproduce the experimental rotational constants best.

Using an extended and modified version of Rinaldi's GEOMO program [3] with corrections suggested in ref. 4, we have calculated the optimized geometries of fluorobenzenes by CNDO/2 and MINDO/3 methods [5]. It appears to be worthwhile to compare our results on dipole moments with those given in ref. 1. The values obtained are listed in Table 1 together with *ab initio* results available in the literature [6].

From inspection of the data shown the following conclusions can be drawn.

(1) Our CNDO/2 dipole moments calculated at geometries optimized by the same method are intermediate between the values obtained at "standard" and " r_0 " geometries reported in ref. 1. Our values agree well (within ± 0.03 debye) with the arithmetic mean of the two values given by Doraiswamy and Sharma.

(2) All theoretical data shown in Table 1 are calculated at geometries optimized by the respective quantum chemical method. Thus, it is possible to compare the methods used from the point of view of how they reproduce dipole moments when no corrections are applied to the theoretical results (e.g., the optimized geometries are not corrected for systematic errors). This comparison leads to the conclusion that the performance of the *ab initio* calculations (using 4-21 basis sets) is the worst and that of MINDO/3 is the best. This observation supports the claim of Dewar [7] that for certain classes of molecules semiempirical methods reproduce electronic structures better than *ab initio* methods with small or medium size basis sets.

TABLE 1

Calculated and experimental dipole moments of fluorobenzenes (in debye)

Substituents	Ab initio ^a	CNDO/2 ^b	MINDO/3 ^b	Experimental ^c
1-F-	2.24 ^d	1.71	1.83	1.63 (3)
1,2-diF-	(3.7) ^e	3.01	2.94	2.59 (2)
1,3-diF-	2.23	1.70	1.79	1.51 (2)
1,2,3-triF-	4.34	3.50	3.27	(2.9) ^e
1,2,4-triF-	(2.1) ^e	1.74	1.61	1.39 (3)
1,2,3,4-tetraF-	(3.6) ^e	3.03	2.70	2.42 (5)
1,2,3,5-tetraF-	(2.1) ^e	1.80	1.49	1.46 (6)
1,2,3,4,5-pentaF-	2.11	1.78	1.47	1.44 (3)

^aValues taken from ref. 6, calculated at ab initio optimized geometries using 4-21 basis sets. ^bPresent results, calculated at geometries optimized by the respective methods. ^cSee ref. 1 for references, the estimated standard errors in the last digits are given in parentheses. ^dNote that assuming $r_{CH} = 108$ pm, $r_{CC} = 140$ pm, $r_{CF} = 133$ pm and all angles 120° $\mu = 2.21$ D and $\mu = 0.93$ D are obtained [8] with 4-31G and STO-3G basis sets, respectively. ^eEstimated values, see text.

(3) Based on the trends in the CNDO/2 results one can predict data not available in the literature; these estimated dipole moments are given (in parentheses) in Table 1. While such estimation of ab initio results might be realistic because CNDO/2, with its original parametrization, is aimed to

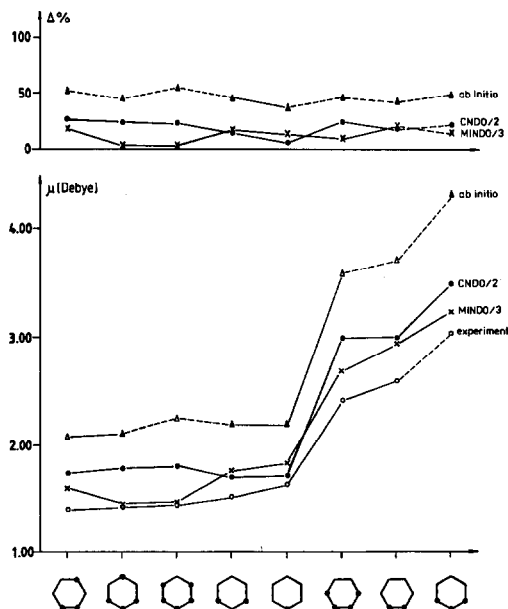


Fig. 1. The calculated and experimental dipole moments of fluorobenzenes (a) and the relative error (Δ) in the calculated values (b). (The positions of fluorination are denoted by the bold points on the benzene rings.)

mimic ab initio STO-3G results, the "experimental" dipole moments predicted in this way may well be in error.

(4) The regularity of the error in the calculated dipole moments can be judged from Fig. 1, where the relative errors, Δ , are also given

$$\Delta = 100(\mu_{\text{calc}} - \mu_{\text{exp}})/\mu_{\text{exp}}$$

For ab initio results, unfortunately, nothing can be discussed on the regularity of the errors, due to lack of appropriate data. Using extrapolated data, however, the mean relative error in dipole moments computed by 4-21 basis set can be estimated at 47%.

The average error in CNDO/2 computed dipole moments is around 20%, and it is quite constant for this class of molecules. The expected error in μ can be set to $20 \pm 5\%$; the only outlier is the monofluorobenzene.

The systematicity of relative errors in dipole moments is also characterized for MINDO/3. The overall mean error is 11%, which after leaving out the two outliers (1,2,3,5-tetrafluorobenzene and pentafluorobenzene), for which the error is surprisingly small, increases to 14%. The expected error is $15 \pm 4\%$.

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