Dipole Moments of Hexamethylbenzene and Hexamethyl-"Dewar Benzene"

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Summary In accordance with CNDO calculations, hexamethyl-"Dewar benzene" has a finite dipole moment, whilst the moment of hexamethylbenzene is zero.

AN all-electron treatment of "Dewar benzene" has been carried out by Berthier, Meyer, and Praud[1] who found that the charge component of the dipole moment was almost cancelled by its polarization component, leading to the very low total calculated moment of 0·16 D. As it is known that all-valence-electron calculations of the CNDO type[2] are well suited to the calculation of dipole moments,[3] we applied this method to "Dewar benzene," using the program written by Clark and Ragle.[4] Dipole moments were computed from overlap populations and net charges[5] thus obtained. The results of the population analysis for this hydrocarbon, based on the geometry reported for its hexamethyl derivative,[6] are shown in the Figure. They are similar to the all-electron values,[1] but lead to a lower charge component of the dipole moment, −0·209 D† (*vs.* −0·448 D). The polarization component, however, is now found to be −0·558 D (*vs.* + 0·287 D) and therefore *enhances* the charge moment, to give a total moment of 0·76 D. Small changes in the flap and bond angles, as well as in the interatomic distances, produce only very slight modifications (a few hundredths of a Debye) in this value. As "Dewar benzene" itself is not stable,[7] the moment of hexamethyl-"Dewar benzene" was determined, using the previously described[8] heterodyne beat method (see Table). Both in benzene and in cyclohexane the moment was 0·5 ± 0·1 D; obviously there is no solvent effect. If the calculated molar refraction[9] is used instead of the measured one, the moment is 0·6 ± 0·1 D. For comparison the moment of hexamethylbenzene was also measured (see Table) under the same conditions in benzene and in cyclohexane, and found to be zero, in agreement with the previously reported value of Tiganik[10] and in contrast to the higher value reported by Meredith and Wright.[11] The determination of small dipole moments is by the nature of the method open to relatively

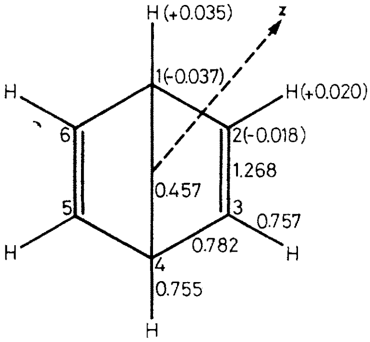

FIGURE. *Population analysis for "Dewar benzene" (CNDO/2 treatment) (the molecule is folded so that* C-2, C-3, C-5, *and* C-6 *are below the plane and the z-axis projects above it).*

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† Moments are reported in the +→ convention.

The experimental dipole moments (30°)

Compound	Solvent	α'	β'	$P_{2\infty}$	MR_{meas}	μ (Debye)
Hexamethyl-"Dewar benzene" ..	Benzene	−0·079	0·193	58·70	52·69	0·55 ± 0·10
Hexamethyl-"Dewar benzene"	Cyclohexane	0·394	−0·103	58·94	53·63	0·51 ± 0·10
Hexamethylbenzene	Benzene	0·217	−0·129	55·68	55·31	0·14 ± 0·10
Hexamethylbenzene	Cyclohexane	0·425	−0·381	53·71	55·09	0·00 ± 0·20

large experimental errors; nevertheless, our results indicate that hexamethyl-"Dewar benzene", unlike hexamethylbenzene, has a finite, albeit small, dipole moment, and thus support the calculations carried out by the all-valence-electron method.

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