On the Magnetic Susceptibility of Hexabenzocoronene and Triphenylene

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Hexabenzocoronene is an extremely stable, pale yellow hydrocarbon. Clar and Ironside suggested that it contains exclusively benzenoid rings interlinked by quasi-single bonds[1]. Afterwards, however, they found an asymmetric effect of the electronic interaction between benzenoid rings, and proposed a formula of hexabenzocoronene consisting of a triphenylene complex and 4 benzenoid rings[2]. Magnetic susceptibility of hexabenzocoronene would be interesting for these points of view, as the effect of the aromatic conjugation should reflect on its value. We measured the magnetic susceptibility of hexabenzocoronene and triphenylene; the samples were provided by C. T. Ironside and M. Zander, respectively.

The purification of the specimens was made by sublimation in vacuo at about 490°C for hexabenzocoronene, and at about 120°C for triphenylene. The magnetic measurement was made by the Gouy method at room temperature. The observed values are as follows. Hexabenzocoronene (M.W. 522.6, density 1.57[3]) :

$-\chi_g\times10^6=0.662\pm0.002$ per gram,
$-\chi_M\times10^6=346.0$ per mole.

Triphenylene (M.W. 228.3, density 1.30).

$-\chi_g\times10^6=0.686\pm0.001$ per gram,
$-\chi_M\times10^6=156.6$ per mole.

The magnetic susceptibilities of related compounds are as follows.

Phenanthrene:

$-\chi_g\times10^6=0.718$; $-\chi_M\times10^6=127.9$

Benzene:

$-\chi_g\times10^6=0.712$; $-\chi_M\times10^6=55.6$

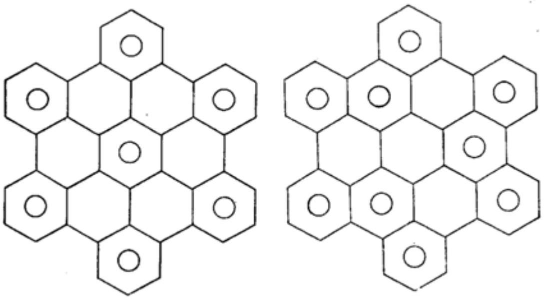
Atomic susceptibility of hydrogen;

$-\chi_M(\text{H})\times10^6=2.93$

Hexabenzocoronene can be presumed as being made of seven benzenoid rings interlinked by quasi-single bonds (Formula 1), or consisting of triphenylene and four benzenoid rings. The expected value of each formula will be respectively,

$$-\chi_M\times10^6=7\chi_M(\text{Benzene})-24\chi_M(\text{H})=318.9$$

$$-\chi_M\times10^6=\chi_M(\text{Triphenylene})+4\chi_M(\text{Benzene})-18\chi_M(\text{H})=326.3$$



Formula (1) Formula (2)

Fig. 1. Hexabenzocoronene

The observed value is higher than those of anticipated formulae. The other formula which is conceivable consists of three phenanthrene rings connected by contact bonds (Formula 2). This leads to the expected value as,

$$-\chi_M\times10^6=3\chi_M(\text{Phenanthrene})-12\chi_M(\text{H})=348.5\ ;\quad -\chi_g\times10^6=0.667$$

This value is very near to the observed one. It is likely that a small effect of the electronic interaction takes place between benzenoid rings, its amount is in the same order as the aromatic conjugation in phenanthrene molecule.

The mean susceptibility of triphenylene was measured by Honda and Ōuchi[4]. Their observed value is $\chi_g=-0.685\times10^{-6}$, which is in good agreement with the present result. From the observed susceptibility and using the empirical formula[5], the principal diamagnetic susceptibilities of triphenylene molecule can be estimated as $K_1=-95.6\times10^{-6}$ and $K_3=-278.6\times10^{-6}$, where K_1 is in the plane of molecule and K_3 is perpendicular to it. This leads to the diamagnetic anisotropy of $\Delta K=-183.0\times10^{-6}$. This value is 3.4 times of the diamagnetic anisotropy of benzene, $\Delta K(\text{Benzene})=-54\times10^{-6}$. The molecular

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[1] E. Clar and C. T. Ironside, *Proc. Chem. Soc.*, **1958**, 150.

[2] E. Clar, C. T. Ironside and M. Zander, *J. Chem. Soc.*, **1959**, 142; E. Clar, *Tetrahedron*, **5**, 98 (1959); Private communication.

[3] A. Halleux, R. H. Martin and G. S. D. King, *Helv. Chim. Acta*, **41**, 1177 (1958).

[4] H. Honda and K. Ōuchi, *Reports of the Resources Research Institute, Japan*, No. 1, 8, (1952).

[5] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953); **29**, 800 (1956).

orbital calculation⁶⁾, however, gave 4.08 for this ratio, which is too large compared with the above value.

Our estimated values of the principal diamagnetic susceptibility are likely to be reasonable from the following reason. Triphenylene crystal is orthorhombic, and its principal susceptibilities along the crystal axes were measured by Banerjee and Guha⁷⁾. Their observed values are $\chi_a = -150.1\times10^{-6}$, $\chi_b = -149.5\times10^{-6}$ and $\chi_c = -174.2\times10^{-6}$. Using these values combined with the above values for K_1 and K_3, we can estimate the orientation of the molecule to the crystal axes. The procedure has been given by Lonsdale and Krishnan⁸⁾. This gives the result that the plane of molecule makes the angle of 50°20′ to the *ab*-plane. This value is in good agreement with the observed angle, 50°30′, by Klug⁹⁾ who made the X-ray crystal analysis of triphenylene.

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Added in Proof:

E. Clar proposed* the other possible formula for hexabenzocoronene, after we had made our communication. He suggested that the induced sextet in the center ring of triphenylene may rotate or oscillate through the ring system of hexabenzocoronene, as if the Formulae 1 and 2 are overlapping with each other. In this case, the induced sextet in triphenylene (the center ring) has magnetic susceptibility of

$$\chi_M(\text{Triphenylene}) - 3[\chi_M(\text{Benzene}) - 2\chi_M(\text{H})] = -7.4\times10^{-6}$$

Three times this value (-22.2×10^{-6}) added to the value for Formula 1, it leads to -341.1×10^{-6} which is near to the observed value.

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7) S. Banerjee and A. C. Guha, *Z. Krist.*, **96**, 107 (1936).

8) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc.*, **A156**, 597 (1936).

9) A. Klug, *Acta Cryst.*, **3**, 165 (1950).

* Private communication.