

# Polarizability and magnetizability anisotropies of trimethylboroxine, $\text{Me}_3\text{B}_3\text{O}_3$ . Comparison of boroxine and benzene ring systems

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## Abstract

Measurements of the Rayleigh depolarization ratio (with and without inclusion of the vibrational Raman contribution) and the temperature dependence of the Cotton–Mouton effect of gaseous trimethylboroxine at 632.8 nm are analyzed to obtain experimental values of the polarizability and magnetizability anisotropies of this species. The polarizabilities and magnetizabilities of trimethylboroxine ( $\text{Me}_3\text{B}_3\text{O}_3$ ) and the symmetrically trimethylated benzene ( $\text{Me}_3\text{C}_6\text{H}_3$ ) are contrasted, and it is inferred that electron delocalization is substantially reduced, possibly even absent, in boroxine as compared to benzene. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

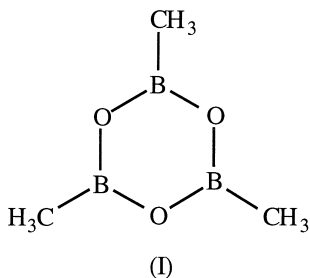
The electric and magnetic properties, and the relative electron delocalizations, of the species benzene, *s*-triazine ( $\text{H}_3\text{C}_3\text{N}_3$ ), borazine ( $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ ) and boroxine ( $\text{H}_3\text{B}_3\text{O}_3$ ) have continued to attract interest [1–6], although boroxine has not yet proved examinable by the relevant experimental methods. In fact, despite the much earlier preparation and structural elucidation of many relatively stable symmetrically trisubstituted boroxines ( $\text{X}_3\text{B}_3\text{O}_3$ ; X = Me [7], OMe, NMe<sub>2</sub>, F, Cl, Br [8], etc.) boroxine itself was not definitively synthesized until 1963, when it was confirmed as a product of the high-temperature (1100–1400 K) reaction of  $\text{H}_2(\text{g})$  with  $\text{B}(\text{s})/\text{B}_2\text{O}_3(\text{l})$  mixtures [9]. At ambient tempera-

tures, however,  $\text{H}_3\text{B}_3\text{O}_3$  is thermodynamically unstable and decomposes to  $\text{B}_2\text{H}_6$  and  $\text{B}_2\text{O}_3$  [10]; and, notwithstanding the fact that under certain conditions the low-pressure gas decomposes sufficiently slowly to permit electron diffraction [11] and some spectroscopic observations [12,13], it seems unlikely that its electric and magnetic properties will be experimentally accessible. In these circumstances, trimethylboroxine ( $\text{Me}_3\text{B}_3\text{O}_3$ , I), in which the electron deficiency of the boron atoms and thereby the reactivity are attenuated by the substituents, is of particular interest as possibly the simplest reasonably stable exemplar of the boroxine ring system. In this Letter, measurements of the Rayleigh depolarization ratio (with and without inclusion of the spurious vibrational Raman contribution) and the temperature dependence of the Cotton–Mouton effect of gaseous  $\text{Me}_3\text{B}_3\text{O}_3$  are reported. Values of the derived polarizabilities and magnetizabilities are summarized and

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compared with those of the symmetrically trimethylated benzene, mesitylene ( $\text{Me}_3\text{C}_6\text{H}_3$ ), and the natures of the boroxine and benzene ring systems are contrasted.



## 2. Theory

For a species that possesses a threefold or higher-order rotation axis so that the molecular polarizability and magnetizability are axially symmetric (i.e.  $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$ ;  $\chi_{xx} = \chi_{yy} \neq \chi_{zz}$ ), the relationship between the Rayleigh depolarization ratio,  $\rho_0 = I_h^v/I_v^v$ , and the polarizability is [14]

$$5\rho_0(3 - 4\rho_0)^{-1} = \left(\frac{\Delta\alpha}{3\alpha}\right)^2 = \kappa^2 \quad (1)$$

in which  $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$  is the polarizability anisotropy and  $\alpha = (\alpha_{zz} + 2\alpha_{xx})/3$  is the mean polarizability. Note, in particular, that Eq. (1) requires that the rotational Raman spectrum be included in and the vibrational Raman spectrum be excluded from the measured intensities [14]. If the species is also diamagnetic, the low-density molar Cotton–Mouton constant,  ${}_mC$ , is, in SI units [15],

$${}_mC = \left[ \frac{2nV_m\mu^2}{3(n^2 + 2)^2} \right] \left[ \frac{n_x - n_y}{B_x^2} \right]_{B_x=0} \quad (2a)$$

$$= \left( \frac{N_A\mu_0^2}{270\varepsilon_0} \right) \left[ \Delta\eta + \frac{2}{3kT}(\Delta\chi\Delta\alpha) \right] \quad (2b)$$

where Eq. (2a) describes the birefringence,  $n_x - n_y$ , for XZ and YZ polarized light that is induced in the gas by the magnetic induction,  $B_x$ , and Eq. (2b) is the connection between the birefringence and the

relevant molecular properties [16];  $\Delta\eta = \eta_{\alpha\beta, \alpha\beta} - \frac{1}{3}\eta_{\alpha\alpha, \beta\beta}$  and  $\Delta\chi = \chi_{zz} - \chi_{xx}$  are the anisotropies in the magnetic hyperpolarizability and the magnetizability, respectively. Other quantities in Eqs. (2a) and (2b) are the isotropic refractive index,  $n$ , the molar volume,  $V_m$ , the permeability,  $\mu$ , the vacuum permeability,  $\mu_0$ , the vacuum permittivity,  $\varepsilon_0$ , the Avogadro constant,  $N_A$ , the Boltzmann constant,  $k$ , and the temperature,  $T$ . From Eq. (2b) it is clear that  ${}_mC$  should exhibit a linear dependence on  $T^{-1}$ , such that the intercept at  $T^{-1} = 0$  defines  $\Delta\eta$  and, provided  $\Delta\alpha$  is known, the slope defines  $\Delta\chi$ .

## 3. Experimental

Samples of trimethylboroxine (Aldrich, > 99%, m.p.  $-38^\circ\text{C}$ , b.p.  $78\text{--}80^\circ\text{C}$ ,  $n_D^{20} = 1.3620$ ,  $\rho_4^{20} = 0.902$ ) were subjected to two freeze–pump–thaw cycles immediately before use. Improved apparatus for measurements of the Rayleigh depolarization ratios of gases and vapours has recently been described [17]. Observations were made at  $87.8^\circ\text{C}$  and  $\approx 35$  kPa, and the results are the averages of repeated determinations, seven with inclusion and five with rigorous exclusion of the extraneous vibrational Raman contribution. The mean polarizability was determined from the Lorenz–Lorentz equation as  $\alpha = (3\varepsilon_0/N_A)[(n^2 - 1)/(n^2 + 2)^2](M/\rho)$ , in which  $n$  and  $\rho$  are the liquid-phase refractive index and density noted above. The high reliability of the value so obtained was easily confirmed by reference to analogous data for triethylboroxine [18] and tables of bond and group refractivities [19,20]. As well, the mean magnetizability, not previously reported, was measured by Kövesdi's static NMR method [21].

Apparatus and procedures detailed elsewhere [15,22,23] were utilized to observe the temperature dependence of the Cotton–Mouton effect of gaseous trimethylboroxine. Measurements of the effect at 632.8 nm were made at 13 temperatures (339.6–431.6 K) and, at each temperature, at  $\approx 9$  pressures (up to  $\approx 52$  kPa); as well, multiple observations were made at each pressure, so that, in total, several hundred measurements were recorded. Under these conditions of pressure and temperature (Eq. (2a)) the definition of the low-density molar Cotton–Mouton

constant can, to a very good approximation, be rewritten as

$${}_mC = \left( \frac{\mu_0^2 \lambda}{27\pi} \right) \left( \int B^2 dl \right)^{-1} \left( \frac{\phi}{V_m^{-1}} \right) \quad (3)$$

in which  $\phi = (2\pi l/\lambda)(n_x - n_y)$  is the retardance induced in light of wavelength  $\lambda$  after traversal of the path length  $l$  through the magnetic induction  $B_x$ . In the present apparatus, the maximum value of the field integral produced by the conventional iron-core electromagnet is  $\int B^2 dl = 3.289 \pm 0.045 \text{ T}^2 \text{ m}$ , and the limit of resolution in the detection of  $\phi$  is typically  $\pm 2 \times 10^{-7} \text{ rad}$ . Values of  $V_m^{-1}$ , the reciprocal of the molar volume, were calculated from the measured pressures and density second virial coefficients,  $B$ , estimated from the single-temperature (98°C) vapour-density data reported by Burg [7], together with a Lennard–Jones potential ( $\epsilon/k = 428 \text{ K}$ ,  $\sigma = 0.829 \text{ nm}$ ) obtained by the usual method [24]. It is relevant here to reiterate the importance in experiments of this kind, where the gas density is monitored by the pressure, of reliable virial coefficients, specially for species as large as (I), for which significant departures from ideal-gas behaviour can be expected. There is, moreover, a subtlety that is well illustrated by the present data: although the corrections at individual temperatures are relatively small ( $\approx 2\text{--}5\%$ ), the variation across the range of temperature conspires to ensure that the correction to

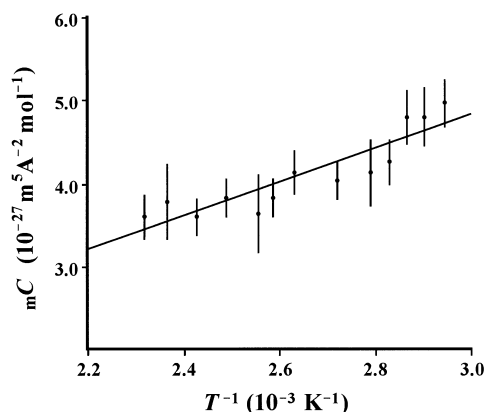


Fig. 1. Temperature dependence of the molar Cotton–Mouton constant of trimethylboroxine at 632.8 nm.

the required property, the slope of the temperature dependence, is considerably larger (9.3%). Accurate gas densities are therefore a prerequisite for accurate molecular properties. Results are summarized in Table 1 and displayed in Fig. 1, where  ${}_mC$  is graphed against  $T^{-1}$ ; the uncertainties shown are the standard deviations derived from the least-squares fitting of straight lines to the density-dependence data.

#### 4. Results and discussion

Table 2 summarizes the experimental values of  $\rho_0$  and  $\alpha$ , and the derived values of  $\Delta\alpha$ ,  $\alpha_{zz}$  and

Table 1

Temperature dependence of the molar Cotton–Mouton constant of trimethylboroxine at 632.8 nm

$T$ (K)	Number of pressures	$p_{\max}$ (kPa)	$B^a$ ( $10^{-6} \text{ m}^3 \text{ mol}^{-1}$ )	${}_mC$ ( $10^{-27} \text{ m}^5 \text{ A}^{-2} \text{ mol}^{-1}$ )
431.6	9	51.9	−1799	$3.60 \pm 0.27$
422.9	9	50.3	−1866	$3.78 \pm 0.45$
412.2	8	44.1	−1951	$3.60 \pm 0.22$
401.9	9	49.8	−2038	$3.83 \pm 0.23$
391.4	7	43.9	−2134	$3.64 \pm 0.46$
386.9	9	46.9	−2175	$3.83 \pm 0.23$
380.2	9	49.6	−2245	$4.14 \pm 0.26$
367.6	9	43.0	−2377	$4.04 \pm 0.23$
358.4	9	42.3	−2486	$4.13 \pm 0.40$
353.4	9	45.5	−2548	$4.26 \pm 0.27$
348.9	9	41.9	−2604	$4.80 \pm 0.32$
344.6	9	42.4	−2657	$4.80 \pm 0.35$
339.6	9	42.8	−2726	$4.97 \pm 0.28$

<sup>a</sup> Density second virial coefficient (see text).

$\alpha_{xx}$ ; the analysis of the temperature dependence of  ${}_mC$  on the basis of Eq. (2b), and the derived values of  $\Delta\eta$  and  $\Delta\chi$ ; the experimental value of  $\chi$ ; and the derived values of  $\chi_{zz}$  and  $\chi_{xx}$ . Points of interest are that for this species, in contrast to others [25], the vibrational Raman contribution is hardly significant; that  $\Delta\eta$ , although poorly determined by the long extrapolation and uncertain intercept at  $T^{-1} = 0$ , is, nevertheless, a significant contributor ( $-23 \pm 15\%$ ) to  ${}_mC$  (300 K); and that both  $\Delta\alpha$  and  $\Delta\chi$  are negative in sign, as expected from the molecular structure (B, O, C coplanar,  $\angle BOB = 112^\circ$  [26]). Note, too, that the value of  $\Delta\chi$  derived by Aroney et al. [27] from measurements of the dilute-solution Kerr and Cotton–Mouton effects of  $\text{Me}_3\text{B}_3\text{O}_3$  in benzene ( $-54.0 \times 10^{-29} \text{ J T}^{-2}$ ) is more than twice as large as that reported here ( $-23.9 \times 10^{-29} \text{ J T}^{-2}$ ), and is certainly incorrect.

Table 3 provides a comparison of the polarizabilities and magnetizabilities of  $\text{Me}_3\text{B}_3\text{O}_3$  and  $\text{Me}_3\text{C}_6\text{H}_3$ , and highlights the fundamental difference between the boroxine and benzene ring systems. In relation to the polarizability, it is obvious that both  $\alpha$  and  $\Delta\alpha$  are considerably smaller in  $\text{Me}_3\text{B}_3\text{O}_3$  than in  $\text{Me}_3\text{C}_6\text{H}_3$ , and that these differences are mainly attributable to a much diminished in-plane polarizability in  $\text{Me}_3\text{B}_3\text{O}_3$  in comparison with  $\text{Me}_3\text{C}_6\text{H}_3$ .

Table 2

Analysis of the Rayleigh depolarization ratio and the temperature dependence of the Cotton–Mouton effect of  $\text{Me}_3\text{B}_3\text{O}_3$  at 632.8 nm

Property	Value
$10^2 \rho_0$ (vib. Raman incl.)	$0.704 \pm 0.004$
$10^2 \rho_0$ (vib. Raman excl.)	$0.695 \pm 0.006$
$\alpha$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ ) <sup>a</sup>	$13.6 \pm 0.1$
$\Delta\alpha$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	$-4.42 \pm 0.05$
$\alpha_{zz}$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	$10.7 \pm 0.1$
$\alpha_{xx}$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	$15.1 \pm 0.1$
intercept ( $10^{-27} \text{ m}^5 \text{ A}^{-2} \text{ mol}^{-1}$ ) <sup>b</sup>	$-1.26 \pm 0.80$
slope ( $10^{-24} \text{ m}^5 \text{ A}^{-2} \text{ mol}^{-1} \text{ K}$ ) <sup>b</sup>	$2.03 \pm 0.30$
$\Delta\eta$ ( $10^{-48} \text{ C m}^2 \text{ V}^{-1} \text{ T}^{-2}$ )	$-3.2 \pm 2.0$
$\Delta\chi$ ( $10^{-29} \text{ J T}^{-2}$ )	$-23.9 \pm 3.5$
$\chi$ ( $10^{-29} \text{ J T}^{-2}$ ) <sup>c</sup>	$-134 \pm 3$
$\chi_{zz}$ ( $10^{-29} \text{ J T}^{-2}$ )	$-150 \pm 4$
$\chi_{xx}$ ( $10^{-29} \text{ J T}^{-2}$ )	$-126 \pm 3$

<sup>a</sup>Calculated from refractive index and density of  $\text{Me}_3\text{B}_3\text{O}_3(l)$  (see text).

<sup>b</sup>See Eq. (2b).

<sup>c</sup>Present work (see text).

Table 3

Comparison of polarizabilities and magnetizabilities of  $\text{Me}_3\text{B}_3\text{O}_3$  and  $\text{Me}_3\text{C}_6\text{H}_3$ <sup>a</sup>

Property	Value	
	$\text{Me}_3\text{B}_3\text{O}_3$	$\text{Me}_3\text{C}_6\text{H}_3$
$\alpha$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	13.6	$17.9^b$
$\Delta\alpha$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	$-4.42 \pm 0.05$	$-9.43 \pm 0.23^b$
$\alpha_{zz}$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	10.7	11.6
$\alpha_{xx}$ ( $10^{-40} \text{ C m}^2 \text{ V}^{-1}$ )	15.1	21.1
$\chi$ ( $10^{-29} \text{ J T}^{-2}$ )	-134	$-153^c$
$\Delta\chi$ ( $10^{-29} \text{ J T}^{-2}$ )	$-23.9 \pm 3.5$	$-108 \pm 6^d$
$\chi_{zz}$ ( $10^{-29} \text{ J T}^{-2}$ )	-150	-225
$\chi_{xx}$ ( $10^{-29} \text{ J T}^{-2}$ )	-126	-117

<sup>a</sup> $\text{Me}_3\text{B}_3\text{O}_3$  = trimethylboroxine,  $\text{Me}_3\text{C}_6\text{H}_3$  = 1,3,5-trimethylbenzene (mesitylene).

<sup>b</sup>Ref. [35].

<sup>c</sup>Ref. [36].

<sup>d</sup>Ref. [37].

Similarly, both  $\chi$  and, especially,  $\Delta\chi$  are smaller in  $\text{Me}_3\text{B}_3\text{O}_3$  than in  $\text{Me}_3\text{C}_6\text{H}_3$ ; but, by contrast, these differences are almost entirely attributable to a much diminished out-of-plane magnetizability in  $\text{Me}_3\text{B}_3\text{O}_3$  in comparison with  $\text{Me}_3\text{C}_6\text{H}_3$ . Unfortunately, a rigorous analysis of these data is not yet possible; but, qualitatively at least, it can safely be inferred that electron delocalization is substantially reduced, possibly even absent, in boroxine as compared to benzene. Although such a conclusion is inconsistent with early suggestions [27–30] of significant delocalization, even ‘aromaticity’, in boroxine, it is, nevertheless, consistent with more recent evidence from a variety of theoretical studies [5,6,31–34].

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