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Can triorganoboroxins exist in a "monomeric" R–B=O form? MNDO calculations and ebulliometric molecular weight determination

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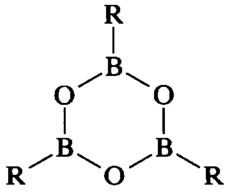
Abstract

MNDO calculations were made for triethylboroxin $(EtBO)_3$ and triphenylboroxin $(PhBO)_3$ using both X-ray determined and optimized geometry of these molecules. The results were compared with hypothetical "monomeric" molecules R–B=O. Calculated energies of trimerization are about -200 kJ mol^{-1} for both compounds and confirm the much higher stability of the "trimer". Ebulliometric determination of molecular weight of triphenylboroxin in 2-pentanone confirms its trimeric character.

Key words: Boroxin; MNDO calculations

1. Introduction



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Triorganoboroxins are the compounds with the well known trimeric structure I, demonstrated by electron diffraction in the gas phase for trimethylboroxin [1], and by X-ray diffraction for crystals of triethylboroxin at low temperature [2] and of triphenylboroxin [3]. The trimeric structure is retained in the complexes formed with electron donors. Such complexes are only formed with strong donors (*e.g.* amines) and only one boron atom of the boroxin is complexed [4]; weaker donors (*e.g.* esters) do not form complexes with boroxins [5]. Asymmetrical boroxins with one or two chelating groups attached to boron atoms also have trimeric structures [6]. Cryoscopic molecular weight determinations for triphenylboroxin in benzene have confirmed its trimeric structure [7]. However, for more bulky substituents (trisubstituted phenyl) the possibility of "dimeric" or "monomeric" structure is suggested [8]. Moreover, ebulliometric measurements in ketones give molecular weights which correspond to dimer for trimesitylboroxin [9] and even to monomer for triphenylboroxin [10]. The aim of the present work was to test the hypothesis that triphenylboroxin exists as the monomeric form in boiling ketones, and to compare the calculated energy of the real $(RBO)_3$ molecule with that of the hypothetical "monomeric" R–B=O form.

2. Results and discussion

2.1. Ebulliometric measurements

The molecular weight (306 ± 7) of triphenylboroxin was determined ebulliometrically in 2-pentanone. This compares well with the 311.7 calculated for $(PhBO)_3$ and confirms the "trimeric"character of this compound in boiling ketone.

Lower values of the molecular weight reported for this compound when determined ebulliometrically in acetone [10] may be due to hydrolysis. The molality of the solution in ebulliometric measurement is about 0.1 mol kg^{-1}. Hence, a water content of about 0.2% is sufficient for full hydrolysis of boroxin with the formation of phenylboronic acid $PhB(OH)_2$. Even smaller contents of water in acetone (which is harder to dehydrate than higher ketones) may cause the partial hydrolysis of triphenylboroxin, and this might be the reason for the reported lower molecular weight.

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TABLE 1. Results of MNDO calculations for triethylboroxin [a]

	Trimer (exp)	Trimer (opt)	Monomer
Bond length (Å)			
B_1O_1	1.3801	1.3811	1.1762
B_1O_2	1.3871	1.3851	–
B_1C_α	1.5651	1.5798	1.5345
$C_\alpha C_\beta$	1.5240	1.5340	1.5466
$C_\alpha H_\alpha$	1.1022 [b]	1.1139	1.1123
$C_\beta H_\beta$	1.1022 [b]	1.1092	1.1090
Angles (deg)			
$B_1O_1B_3$	121.60	124.65	–
$O_1B_1O_2$	118.40	115.35	–
$O_1B_1C_\alpha$	121.70	124.42	179.00
$B_1C_\alpha C_\beta$	116.80	117.03	113.34
Charges			
O_1	−0.2248	−0.2506	−0.1341
B_1	0.1521	0.1641	−0.0530
C_α	0.0024	0.0190	0.0892
C_β	0.0334	0.0322	0.0263
Enthalpy of formation (kJ mol^{-1})			
	−1408.7	−1385.7	−392.3

[a] $(EtBO)_3$: trimer (exp)—geometry from X-ray [2], trimer (opt)—optimized geometry, EtBO: optimized geometry of monomer. Numbering of the atoms is given in Fig. 1. [b] Assumed as a typical value for $(sp)^3C$–H bond

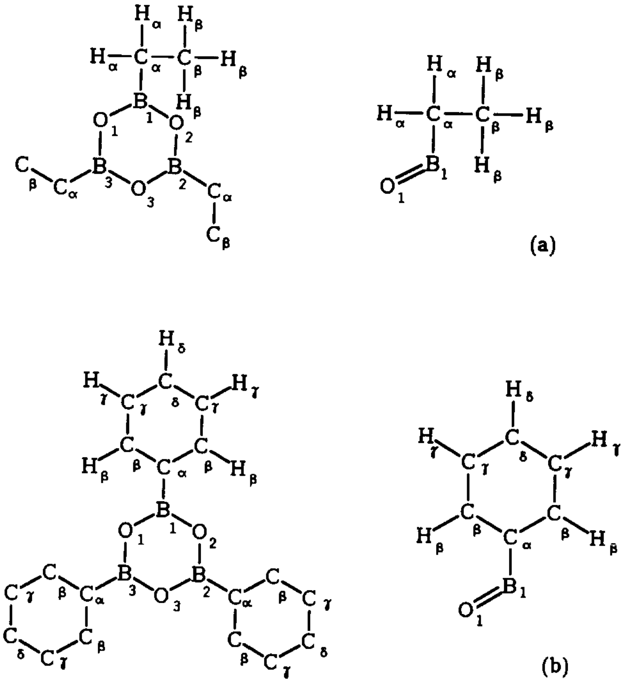

Fig. 1. Numbering of the atoms used in Table 1 (a) and in Table 2 (b).

2.2. MNDO calculations

The results of MNDO calculations are collected in Table 1 for triethylboroxin and in Table 2 for triphenylboroxin.

Calculations used the molecular geometry as determined by Boese *et al.* for triethylboroxin [2] and by Brock *et al.* for triphenylboroxin [3] (trimer exp), and with full optimization of the geometry of the molecules with respect to total energy (trimer opt). The same calculations were made for hypothetical R–B=O molecules with optimization of its geometry (monomer).

The bond lengths and angles obtained from fully optimized calculations for $(EtBO)_3$ and $(PhBO)_3$ agree well with those determined by X-ray measurements. In the case of $(PhBO)_3$ a significant difference is observed only in the angle between the planes of the boroxin ring $(BO)_3$ and the phenyl rings. This difference may be due to possible effects of crystal packing conformation of the molecule [3] so the results of the calculations should be compared with the experimental geometry for the gas phase.

The difference between the energies calculated for "trimer" in both cases (trimer exp and trimer opt) for $(EtBO)_3$ is small: about 23 kJ mol^{-1}. The greater value for $(PhBO)_3$ (about 110 kJ mol^{-1}) can be caused by the conformation changes mentioned above.

The results confirm the reliability of the method used for calculations.

TABLE 2. Results of MNDO calculations for triphenylboroxin [a]

	Trimer (exp)	Trimer (opt)	Monomer
Bond length (Å)			
B_1O_1	1.378	1.383	1.177
B_2O_1	1.386	1.383	–
B_1C_α	1.544	1.557	1.501
$C_\alpha C_\beta$	1.400 [b]	1.407	1.409
$C_\beta H_\beta$	1.040 [b]	1.091	1.090
Angles (deg)			
$B_1O_1B_2$	121.8	123.8	–
$O_1B_2O_3$	117.3	116.2	–
$C_\alpha B_1O_2$	120.6	121.9	180.0
$C_\beta C_\alpha B_1$	120.0	120.8	120.4
$C_\beta C_\alpha B_1O_1$	3.1	58.3 [c]	–
Charges			
O_1	−0.2247	−0.2357	−0.1350
B_1	0.1741	0.2158	0.0140
C_α	−0.0915	−0.0620	−0.0166
C_β	0.0092 [c]	−0.0149	−0.0069
C_γ	−0.0864 [c]	−0.0747	−0.0751
C_δ	−0.0264	−0.0401	−0.0282
Enthalpy of formation (kJ mol^{-1})			
	−785.8	−898.5	−223.5

[a] $(PhBO)_3$: trimer (exp)—geometry from X-ray [3], trimer (opt)—optimized geometry, PhBO: optimized geometry of monomer. Numbering of the atoms is given in Fig. 1. [b] Phenyl rings treated as rigid groups [3]. [c] Mean value.

The trimerization energy, calculated as:

$$\Delta E = E_{trimer} - 3E_{monomer}$$

in the case of $(EtBO)_3$ is about -232 kJ mol^{-1} (for experimental trimer geometry) and about -209 kJ mol^{-1} (for optimized trimer geometry), and in the case of $(PhBO)_3$ -115 and -228 kJ mol^{-1}, respectively. These results confirm the much greater stability of trimeric form for both compounds.

3. Experimental section

Triphenylboroxin was obtained from phenylboronic acid (Heyl, Germany) by dehydration with toluene and crystallized from benzene, (mp 218–220°C). 2-Pentanone (BDH) was dried with 4A molecular sieves and distilled in argon atmosphere, bp 102–102.5°C at atmospheric pressure.

Molecular weight determination was made by differential method using modified Świętosławski ebulliometers [11] at atmospheric pressure of purified argon. Temperature was measured by Beckmann thermometers of 0.005 K resolution. Calibration was with naphthalene.

MNDO calculations were carried out with MOPAC (version 5.0) [12] for IBM PC. Parametrization for C, H, O atoms was taken from [13] and for B atoms from [14].

References

1 S.H. Bauer and J.Y. Beach, *J. Am. Chem. Soc., 63* (1941) 1394.
2 R. Boese, M. Polk and D. Bläser, *Angew. Chem., 99* (1987) 239.
3 C.P. Brock, R.P. Minton and K. Niedenzu, *Acta Cryst., C43* (1987) 1775.
4 M. Yalpani and R. Boese, *Chem. Ber., 116* (1983) 3347.
5 A. Sporzyński, unpublished results.
6 R. Köster, K. Angermund, A. Sporzyński and J. Serwatowski, *Chem. Ber., 119* (1986) 1931.
7 R.C. Kinney and D.F. Pontz, *J. Am. Chem. Soc., 58* (1936) 197.
8 B. Pachaly and R. West, *J. Am. Chem. Soc., 107* (1985) 2987.
9 R.T. Hawkins, W.J. Lennarz and H.R. Snyder, *J. Am. Chem. Soc. 82* (1960) 3053.
10 G. Nencetti, S. Zanelli and G. Nardini, *Ann. Chim. (Rome), 53* (1963) 1875.
11 M. Rogalski and S. Malanowski, *Fluid Phase Equilibria, 5* (1980) 97.
12 J.J.P. Stewart, MOPAC Manual, A General Molecular Orbital Package, Edn. 5. F.J. Seiler Research Laboratory, US Air Force Acad., Colorado Springs, 1987.
13 M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99* (1977) 4899.
14 M.J.S. Dewar and M.L. McKee, *J. Am. Chem. Soc., 99* (1977) 5231.