

## The Structure of the Tri-iodide Ion

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THE tri-iodide ion bond-lengths are reported as equal in crystals of  $\text{As}(\text{C}_6\text{H}_5)_4\text{I}_3^1$  and  $\text{HI}_3 \cdot 2\text{C}_6\text{H}_5\text{-CONH}_2^2$  but unequal in  $\text{NH}_4\text{I}_3^3$  and  $\text{CsI}_3^4$ . In all cases the ion departs by a few degrees from linearity. Electrostatic theories<sup>5,6</sup> of the ion bonding imply unequal lengths, whereas resonance<sup>7,8</sup> and molecular orbital<sup>9,10</sup> treatments predict a linear ion with equal bonds ( $D_{\infty h}$ ). The bending of the ion in crystals has been regarded<sup>9</sup> as due to

the distortion caused by the lattice environment.

We have recently recorded the low-frequency infrared spectrum of  $\text{Bu}_4\text{NI}_3$  in benzene, nitrobenzene, and pyridine solution, and also as a Nujol mull. The solutions show a strong band at  $140 \text{ cm.}^{-1}$  (benzene),  $138 \text{ cm.}^{-1}$  (nitrobenzene),  $139 \text{ cm.}^{-1}$  (pyridine), and  $133 \text{ cm.}^{-1}$  (mull).  $\text{Bu}_4\text{NI}$  is clear in this region. The systems show no absorption around  $109\text{--}113 \text{ cm.}^{-1}$ , the position of

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<sup>2</sup> M. J. Reddy, K. Knox, and M. B. Robin, *J. Chem. Phys.*, 1964, **40**, 1082.

<sup>3</sup> R. C. L. Mooney, *Z. Krist.*, 1935, **90**, 143.

<sup>4</sup> H. A. Tasman and K. H. Boswijk, *Acta Cryst.*, 1955, **8**, 59.

<sup>5</sup> A. E. van Arkel and J. H. de Boer, *Rec. Trav. chim.*, 1928, **47**, 593.

<sup>6</sup> M. Davies and E. Gioynne, *J. Amer. Chem. Soc.*, 1952, **74**, 2748.

<sup>7</sup> R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, 1951, **73**, 4321.

<sup>8</sup> G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446.

<sup>9</sup> E. E. Havinga and E. H. Wiebenga, *Rec. Trav. chim.*, 1959, **78**, 724.

<sup>10</sup> M. B. Robin, *J. Chem. Phys.*, 1964, **40**, 3369.

the only Raman band<sup>11</sup> due to the  $I_3^-$  ion. The vibration spectra therefore support the linear centrosymmetric  $D_{\infty h}$  structure.

Robin,<sup>10</sup> by a simple molecular-orbital treatment, has shown that the electronic spectrum of  $I_3^-$  could result from a slightly bent ion. As spectra in crystal and solution are similar, this implies a bent ion in solution—thus an angle of  $171^\circ$  is calculated for the ion in aqueous solution. The bending is ascribed to van der Waals interaction with the solvent. We have examined our spectra to determine whether this amount of bending would be detectable. Using bond dipoles, the symmetric stretching intensity would be rather less than 1% of the antisymmetric stretching

intensity. This is about the limit of sensitivity of the spectrometer at the frequency. Although on Robin's theory the bond angle, and also the symmetric stretching intensity, would be very solvent-sensitive, no evidence of this band is found in any of the four systems examined.

Assuming a  $D_{\infty h}$  structure, the stretching and interaction force constants are  $0.71$  and  $0.23 \times 10^6$  dyne  $\text{cm.}^{-1}$  respectively. The stretching force constant is reduced to  $0.42$  of that of the  $I_2$  molecule. In comparison, the stretching force constant of the  $Br_3^-$ ,<sup>11</sup> only  $0.38$  of that of  $Br_2$ , reflects the lesser stability of the  $Br_3^-$  ion compared to that of the  $I_3^-$  ion.

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<sup>11</sup> W. B. Person, G. R. Anderson, J. N. Forderwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, 1961, **35**, 908.