Microwave Spectrum of *o*-Benzoquinone

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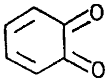
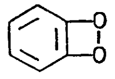
Summary Results of analysis of the microwave spectrum of *o*-benzoquinone are consistent with its assuming the classical *o*-quinonoid structure in the gas phase; its dipole moment is $14{\cdot}1 \times 10^{-30}$ C m.

o-Benzoquinone is the simplest conjugated *ortho*-dione and can exist in either a quinonoid (I) or a benzenoid (II) form.

Two modifications of *o*-benzoquinone have been reported.[1] One is a red crystalline form stable at room temperature and is considered to have the quinonoid structure. The second is a colourless form thought to be due to the benzenoid structure; it is stable at low temperatures and changes into the red species at room temperature.



(I)



(II)

An X-ray diffraction analysis[2] of the red form indicated a structure with differing C–C bond lengths as would be expected for the quinonoid species. Analysis of the microwave spectrum could identify the species present in the vapour phase at room temperature.

The sample of *o*-benzoquinone was prepared by oxidation of guaiacol with sodium metaperiodate.[3] The molecular structure derived from the X-ray analysis was used to predict an approximate spectrum which was recognizably similar to the observed spectrum. The latter was then analysed to give $A = 3{\cdot}30990$, $B = 2{\cdot}49541$, $C = 1{\cdot}42195$ GHz. Measured frequencies of about 20 transitions agreed to within 0·4 MHz of a rigid rotor spectrum calculated using these constants. Calculations using firstly the geometry of the C_6H_4 fragment derived from the X-ray analysis and secondly the C_6H_4 geometry of a regular benzene ring together with the experimental value of the A rotational constant yielded an O–O distance of 2·8 and 2·9 Å respectively. This evidence suggests that the quinonoid structure rather than the benzenoid structure, which would be expected to have an O–O distance of not more than 1·5 Å, is present in the vapour phase.

A determination of the complete molecular structure would require analysis of the spectra of several isotopic species. However, the results obtained here are in substantial agreement with the rotational constants $A = 3{\cdot}3401$, $B = 2{\cdot}4764$, $C = 1{\cdot}4220$ GHz derived from the X-ray analysis, lending support to the conclusion that the quinonoid structure is present in the vapour phase.

The dipole moment of *o*-benzoquinone was found to be $\mu = \mu_a = (14{\cdot}11 \pm 0{\cdot}07) \times 10^{-30}$ C m ($4{\cdot}23 \pm 0{\cdot}02$ Debye) from Stark effect measurements on $2_{11} \leftarrow 1_{10}$, $3_{12} \leftarrow 2_{11}$, and $3_{03} \leftarrow 2_{02}$ transitions.

The results of solution measurement[4] ($17{\cdot}01 \times 10^{-30}$ C m) are appreciably different from the present gas-phase measurements. LCAO calculations ($16{\cdot}18 \times 10^{-30}$ C m,[5] $13{\cdot}17 \times 10^{-30}$ C m,[6] $15{\cdot}61 \times 10^{-30}$ C m[7]) are in reasonable agreement with the Stark effect measurement. It is also interesting to note that the dipole moment ($15{\cdot}41 \times 10^{-30}$ C m[8]) for two *trans*-acrolein molecules placed side by side as in *o*-benzoquinone is in close accord with the observed *o*-benzoquinone moment.

The inertial defect of $0{\cdot}203 \pm 0{\cdot}001 \times 10^4$ a.m.u. pm^2 is somewhat larger than that for typical planar cyclic systems but nevertheless implies that *o*-benzoquinone is essentially planar in the gas phase.

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[1] W. M. Horspool, *Quart. Rev.*, 1969, **23**, 204.
[2] A. L. Macdonald and J. Trotter, *J.C.S. Perkin II*, 1973, 476.
[3] E. Adler and R. Maguusson, *Acta Chem. Scand.*, 1959, **13**, 505.
[4] S. Nagakura and A. Kuboyama, *J. Amer. Chem. Soc.*, 1954, **76**, 1003.
[5] J. C. Berry, *Theor. Chim. Acta*, 1965, **3**, 363.
[6] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1966, **88**, 2367.
[7] G. J. Gleicher, D. F. Church, and J. C. Arnold, *J. Amer. Chem. Soc.*, 1974, **96**, 2403.
[8] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104.