Crystal Structure of Tropone at −60 °C

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Summary Tropone shows pronounced bond alternation but is nevertheless approximately planar.

ALTHOUGH there has been a number of attempts to relate the chemical and physical properties of tropone to structural models, and extensive theoretical calculations have been reported over the past twenty years, it is surprising that no accurate three-dimensional *X*-ray analysis has been published. At room temperature, tropone is a liquid (m.p. −7 °C), unstable to light and air. We have undertaken the analysis of crystalline tropone at −60 °C.

Crystal data: C_7H_6O, $M = 106{\cdot}1$, monoclinic, $a = 6{\cdot}11(3)$, $b = 7{\cdot}91(3)$, $c = 12{\cdot}41(6)$ Å, $\beta = 107{\cdot}5(2)°$, $U = 572$ Å^3, $Z = 4$, $D_c = 1{\cdot}23$. Space group Pc (C_s^2, No. 7) by systematic absences and analysis. 801 photographic intensities, of which 80 were 'zero', were estimated visually (Weissenberg technique). R 5·4 for all reflexions, 4·9 for observed reflexions only. The analysis, by direct methods, was complicated by the occurrence of two molecules per asymmetric unit. Moreover, the rings of these two molecules were related by the pseudo-symmetry operation of a two-fold screw axis (see Figure).

Each of the crystallographically-independent molecules exhibits an idealised plane of mirror symmetry which contains the carbonyl group and bisects the C(4)–C(5) bond. Departures from this symmetry, see Figure, and the differences of bond lengths and angles between the molecules are within experimental error [σ(C–C) = 0·009 Å]. To a first approximation only the molecules are planar; however both show the same systematic distortion from exact planarity and this is in the same sense as is observed in cycloheptatriene.[1] A similar, but some three times greater, distortion from planarity is observed in tricarbonyltroponechromium.[2] Thus comparison establishes that complex formation with $Cr(CO)_3$ results in a greater departure from planarity in the case of tropone in direct contrast to the case of cycloheptatriene.[3]

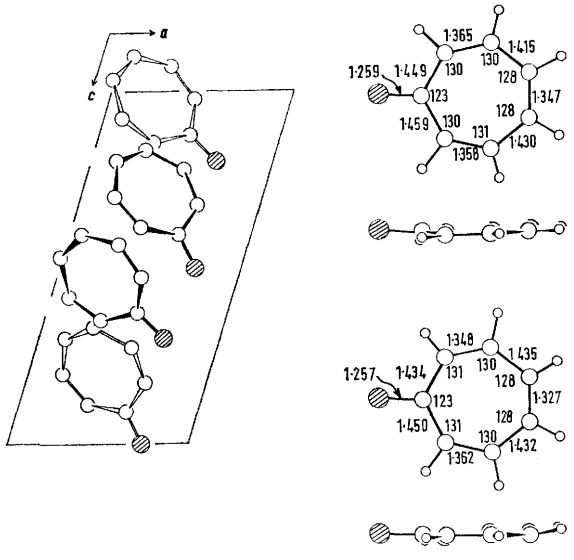

FIGURE. *Packing of independent molecules in unit cell and* (right) *bond lengths and angles for both molecules in the crystal form of tropone.*

The C–C bond distances show a clear distinction between the formally-single and -double bonds. However the double bonds appear marginally longer, and the single bonds

slightly shorter, than the usually accepted values.[4] The C–O distance is also slightly longer than that normally quoted for a ketonic bond.[4] The bond-lengths are in good agreement with those quoted for 3-azidotropone.[5] They should also be compared with those predicted from CNDO/2 calculations[6] and are in accord with the prediction from these calculations that tropone has a negligible resonance stabilisation energy. Our results are uncorrected for molecular thermal motion; comparison with 3-azidotropone suggests that such corrections will not exceed +0·010 Å for all the bonds shown. The results of this crystal structure analysis are at variance with those of a much earlier electron diffraction study[7] which seemed to support the delocalised zwitterion representation. It would appear from our examination that such a form can contribute little to the averaged structure at −60 °C.

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