

The Crystal Structure of a Meisenheimer Complex: the Potassium Methoxide Adduct of 4-Methoxy-5,7-dinitrobenzofurazan

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RECENT evidence^{1,2} indicates that Meisenheimer complexes, the stable intermediates in nucleophilic aromatic substitution reactions, are covalent molecules rather than charge-transfer complexes with the alkoxide ion bonded to a carbon atom of the ring. We report our three-dimensional X-ray diffraction study of the potassium methoxide adduct of 4-methoxy-5,7-dinitrobenzofurazan, the first crystal structure determination of a Meisenheimer complex of a substituted benzofurazan. The compound exhibits some novel ring distortions which can be attributed to the difference in electron-withdrawing power of the substituents.

$Z = 8$. 7048 Independent reflections were measured on a Datex automated General Electric diffractometer with Zr-filtered Mo- K_{α} ($\alpha_1 = 0.70926 \text{ \AA}$) radiation using the stationary-crystal stationary-counter technique. Of these, 4013 were considered to be observed and were used in the refinement. The structure was solved directly from the normalized structure factor magnitudes using the symbolic addition procedure. A series of computer programs,⁶ FAME-MAGIC-LINK-SYMP, was used to carry out the procedure. The structure was refined by Fourier analysis and full-matrix least-squares to $R = 0.066$. A view of the molecule showing the mean intramolecular distances is given in the Figure.

The crystal structure consists of K^+ and $[(\text{MeO})_2\text{C}_6\text{H}(\text{NO}_2)_2\text{N}_2\text{O}]^-$ ions separated by van der Waals forces. The presence of two molecules in the asymmetric unit allows the geometry of the complex to be measured twice. Within the limits of experimental error, the four C(ring)-O(methoxy) bond distances are equal with a mean of $1.415 \pm 0.006 \text{ \AA}$, in agreement with the value observed in the 2,4,6-trinitrophenetole complex.⁴ The mean of the O(methoxy)-C(methyl) bond-lengths is $1.426 \pm 0.007 \text{ \AA}$. Therefore, the C(ring)-O(methoxy) and O(methoxy)-C(methyl) bonds are equal within the experimental error, demonstrating the covalent nature of the methoxy-ring bonds and the sp^3 hybridization of the ring carbon atom.

The distortions observed in the benzene ring provide a novel example of substitution effects on the ring. In the 2,4,6-trinitrophenetole ion,⁴ the benzene ring distances were symmetrical with respect to the tetrahedral ring carbon atom. In the present case, the two sides of the ring are different. The benzofurazan ring appears to have a stronger electron-withdrawing effect than the two nitro-groups. The effect of the various groups is localized and not distributed equally around the ring.

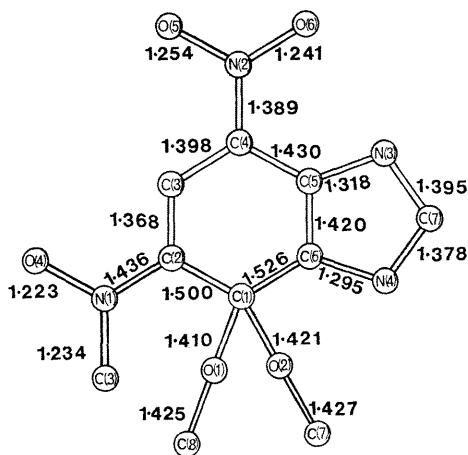


FIGURE. A model of the $[(\text{MeO})_2\text{C}_6\text{H}(\text{NO}_2)_2\text{N}_2\text{O}]^-$ ion with averaged bond distances. The plane defined by C-1-O-1-O-2-C-7-C-8 makes an angle of 89° with the ring.

The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^2) with cell constants: $a = 15.152$, $b = 9.307$, $c = 17.780 \text{ \AA}$, $\beta = 106.22^\circ$; $D_c = 1.712 \text{ g./cm.}^3$, D_m (floatation) = 1.718 g./cm.^3 .

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