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The Structure of Meisenheimer Complex as Determined by X-ray Crystal Analysis

Hideo UEDA,[*1] Noriyoshi SAKABE and Jiro TANAKA[*2]

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya

and Akio FURUSAKI

Faculty of Science, Kwansei Gakuin University, Nishinomiya, Hyogo

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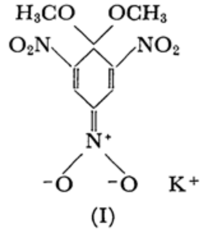
The structure of the Meisenheimer complex has been determined by the X-ray method. The complex is characterized by a symmetrical structure, in which the two methoxyl groups are nearly equivalent to each other. The results showed a peculiar shape of the reaction intermediate, the substituted carbon atom is transformed into a tetrahedral shape, while the planarity of the whole molecule is kept with an increased conjugation between the nitro group and the ring system.

The Meisenheimer complex, a reaction intermediate in a nucleophilic substitution reaction, has been widely investigated from both chemical and structural points of view. The structural formula (I) proposed as an explanation of the chemical behavior has been discussed by many people[1-5]; recent nuclear magnetic resonance results[6,7] indicate that the two methoxyl groups are equivalent in solution.



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[*1] Present address: Ube Industries Ltd., Ube, Yamaguchi

[*2] To whom any correspondence should be mailed.

1) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

2) L. K. Dyall, *J. Chem. Soc.*, **1960**, 5160.

3) S. Nagakura, *Terahedron*, **19**, Suppl. **2**, 361 (1963).

4) R. Foster and R. K. Mackie, *J. Chem. Soc.*, **1963**, 3796.

5) M. R. Crampton and V. Gold, *ibid.*, **1964**, 4293.

6) M. R. Crampton and V. Gold, *Chem. Commun.*, **1965**, 256.

7) K. L. Servis, *J. Am. Chem. Soc.*, **89**, 1507 (1967).

The crystal of the complex was first isolated by Meisenheimer,[1] while preliminary structure reports have been presented by us[8] and by Destro, Gramaccioli and Simonetta[9] independently. The present paper will describe the full details of the structure of the 1,1′-dimethoxy-2,4,6-trinitrobenzene potassium dihydrate, ($K^+[C_6H_2(NO_2)_3(OCH_3)_2]^- \cdot 2H_2O$).

Experimental

The material was obtained from the reaction of picryl chloride and potassium methoxide. It was recrystallized from an acetonitrile solution. The crystal includes two molecules of water, which has been confirmed by the elemental analysis (Found: C, 27.36; H, 3.91; N, 11.96%. Calcd for $C_8H_8O_8N_3K \cdot 2H_2O$: C, 27.50; H, 3.45; N, 12.00%.). The unit-cell dimensions and space group were determined by the oscillation and by Weissenberg photographs. The three-dimensional intensity data were collected using Cu*Kα* radiation with a Weissenberg camera by the multiple-film technique for layer lines 0—5 about the b axis and for layer lines 0—5 about the c axis. The intensities were measured visually, and 1897 independent data were obtained. The scaling of the intensity data, including corrections for different films, corrections for Lorentz and polarization factors, and Wilson's statistical-data analysis, were performed on the HITAC 5020 computer at the Computation center of the University of Tokyo. No corrections were made for either absorption or extinction, since the crystal used was sufficiently small in size for these effects to be neglected.

Crystal Data. $K^+[C_6H_2(NO_2)_3(OCH_3)_2]^- \cdot 2H_2O$ MW 348, Triclinic, $P\bar{1}$ $a=9.36\pm0.02$, $b=10.84\pm0.02$, $c=7.40\pm0.02$ Å, $\alpha=87°40'$, $\beta=106°43'$, $\gamma=102°45'\pm20'$, $Z=2$.

The crystal density, determined by the floatation method in a carbon tetrachloride and methylene iodide mixture, was 1.64 g·cm^{-3}, while the calculated value was 1.65 g·cm^{-3}. No systematic absent spectra have been found.

Structure Analysis. A three-dimensional Patterson synthesis was made using the observed structure factors. The position of the potassium atom was easily found after ascertaining the highest peak. By the aid of the image-seeking method on the Patterson map, we were able to find the location of the benzene ring. At this stage the trial coordinates for all the atoms except the two water molecules were determined, and a least squares refinement with isotropic temperature factors was initiated. After several refinements the *R*-factor was 26%, at this stage the Fourier synthesis was done, and the locations of two water molecules were established. Including the water molecules, the least-squares refinement was then repeated, the *R*-factor was 0.16. Using the anisotropic temperature factors for all the atoms the final *R*-factor was found to be 0.130. The atomic coordinates determined are listed in Table 1, together with the anisotropic temperature factors. The calculated and observed structure factors for all 1897 reflections are kept at the Chemical Society of Japan*[3].

TABLE 1. ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
K- 1	0.1358	0.0567	0.2982	0.0067	0.0030	0.0041	0.0036	0.0007	0.0007
O- 1	0.3150	0.8754	0.3605	0.0039	0.0021	0.0074	−0.0001	0.0011	0.0032
O- 2	0.0966	0.7902	0.4134	0.0041	0.0020	0.0089	0.0017	−0.0030	0.0045
O- 3	0.0544	0.8668	0.0412	0.0110	0.0030	0.0102	0.0069	−0.0051	−0.0066
O- 4	0.0551	0.7243	0.8522	0.0123	0.0075	0.0015	0.0054	0.0029	0.0003
O- 5	0.3574	0.8078	0.7375	0.0090	0.0051	0.0095	0.0034	−0.0046	−0.0060
O- 6	0.3869	0.6182	0.8123	0.0175	0.0056	0.0038	0.0105	0.0063	0.0005
O- 7	0.2412	0.3600	0.0586	0.0133	0.0056	0.0085	0.0068	−0.0092	−0.0026
O- 8	0.3231	0.3164	0.3551	0.0127	0.0026	0.0099	0.0069	−0.0015	0.0021
O- 9	0.8317	0.9903	0.3224	0.0080	0.0050	0.0094	0.0033	−0.0023	0.0044
O-10	0.3248	0.1296	0.0209	0.0097	0.0047	0.0130	0.0027	−0.0095	0.0002
N- 1	0.3478	0.6980	0.6950	0.0063	0.0037	0.0037	0.0019	−0.0011	−0.0002
N- 2	0.0880	0.7663	0.0110	0.0067	0.0048	0.0019	0.0042	−0.0009	−0.0016
N- 3	0.2771	0.3907	0.2277	0.0056	0.0033	0.0119	0.0001	−0.0057	0.0009
C- 1	0.2169	0.7546	0.3590	0.0035	0.0027	0.0053	0.0012	−0.0021	0.0039
C- 2	0.1654	0.6968	0.1676	0.0056	0.0024	0.0055	0.0040	0.0011	0.0047
C- 3	0.1895	0.5840	0.1265	0.0048	0.0026	0.0090	0.0026	−0.0028	0.0047
C- 4	0.2571	0.5085	0.2687	0.0056	0.0023	0.0115	−0.0001	−0.0041	−0.0025
C- 5	0.3052	0.5469	0.4578	0.0045	0.0031	0.0103	0.0017	−0.0010	0.0029
C- 6	0.2876	0.6628	0.4978	0.0045	0.0029	0.0061	−0.0011	−0.0007	0.0016
C- 7	0.4545	0.8732	0.3137	0.0060	0.0059	0.0212	0.0008	0.0019	0.0148
C- 8	0.9678	0.6889	0.4118	0.0006	0.0059	0.0195	−0.0080	−0.0064	0.0065

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8) H. Ueda, N. Sakabe, J. Tanaka and A. Furusaki, *Nature*, **215**, 956 (1967).

9) R. Destro, C. M. Gramaccioli and M. Simonetta, *Nature*, **215**, 389 (1967).

*[3] The complete data of the F_o-F_c table are kept as Document No. 6803 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥600 for photoprints. Pay by check or money order, payable to Chemical Society of Japan.

Results and Discussion

The bond distances and angles in the Meisenheimer complex are shown in Figs. 1 and 2. The standard deviations for atomic positions are tabulated in Table 2, the maximum standard deviation for ring carbon atoms is 0.013 Å, while that for substituent methoxyl groups is 0.016 Å. The standard deviation for the bond length in the benzene ring is 0.017 Å, while the values for the substituents are 0.019 Å.

The most important result concerning the structure is that the two methoxyl groups are perfectly equivalent, this confirms the earlier chemical and spectroscopic evidence concerning the symmetrical structure. The lengths of C(1)–O(1) and C(1)–O(2) bonds are 1.42 Å, normal for saturated compound. The C(7), O(1), C(1), O(2) and C(8) atoms are almost on a plane, which can be represented by the equation $0.4951\,X+0.8618\,Y-0.1106\,Z-1.2544=0$ in which the X, Y, and Z coordinates, in Å units, refer to the orthogonal axes a′, b and c′. The orthogonal axes were b, the crystal axis, a′, the projected a axis (a sin γ), and third axis, c′, perpendicular to a′ and b. The deviations from this plane are shown in Table 3. This plane makes an angle of 87°49′ with the

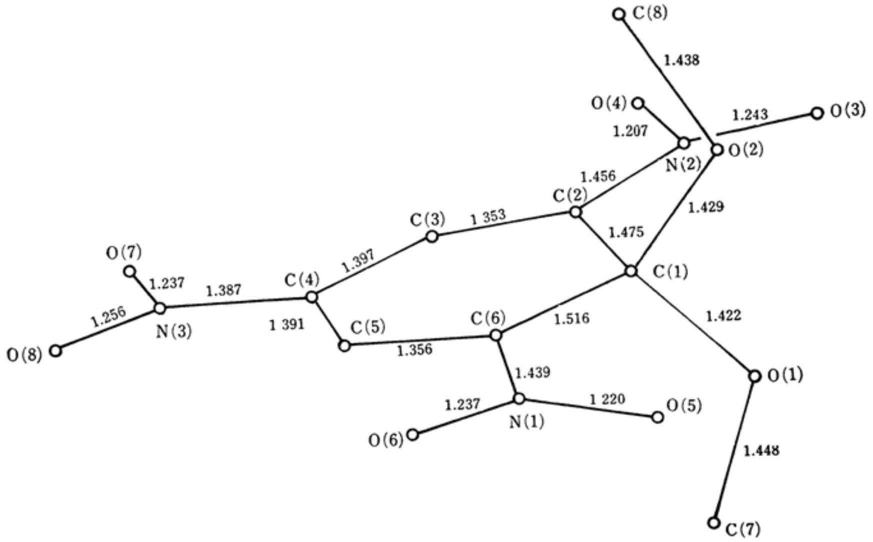


Fig. 1. The bond lengths in Meisenheimer complex.

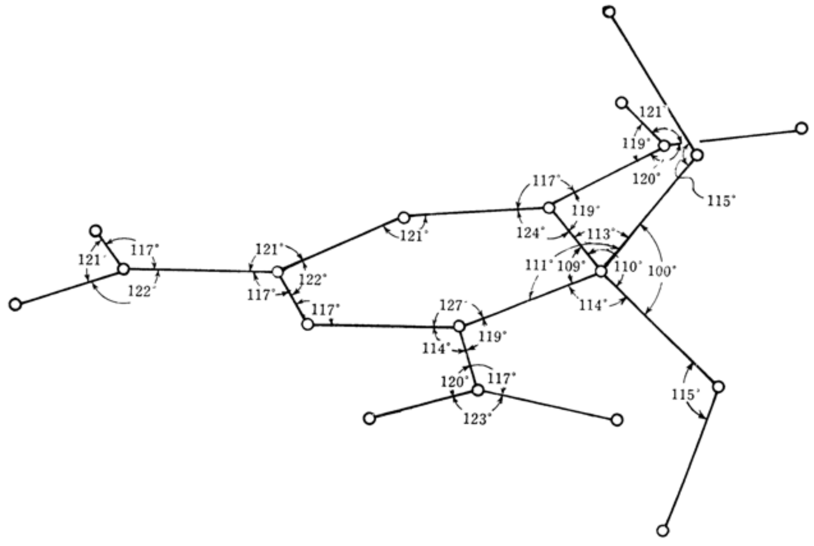


Fig. 2. The bond angles in Meisenheimer complex.

Table 2. Standard deviation of atomic positions (in Å)

Atom	σ(x)	σ(y)	σ(z)
K- 1	0.0026	0.0024	0.0025
O- 1	0.0071	0.0069	0.0077
O- 2	0.0072	0.0070	0.0078
O- 3	0.0093	0.0079	0.0088
O- 4	0.0097	0.0093	0.0081
O- 5	0.0090	0.0087	0.0089
O- 6	0.0108	0.0089	0.0086
O- 7	0.0101	0.0090	0.0089
O- 8	0.0096	0.0079	0.0087
O- 9	0.0086	0.0086	0.0087
O-10	0.0093	0.0087	0.0093
N- 1	0.0095	0.0092	0.0092
N- 2	0.0096	0.0096	0.0090
N- 3	0.0097	0.0095	0.0105
C- 1	0.0099	0.0101	0.0107
C- 2	0.0107	0.0101	0.0110
C- 3	0.0107	0.0105	0.0116
C- 4	0.0115	0.0107	0.0126
C- 5	0.0109	0.0108	0.0120
C- 6	0.0105	0.0105	0.0112
C- 7	0.0127	0.0135	0.0155
C- 8	0.0101	0.0125	0.0141

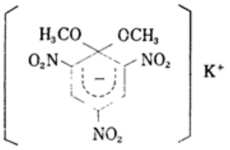
Table 3. The deviation of atoms from the two methoxyl group plane

C-7	−0.009 (Å)
O-1	−0.007
C-1	0.007
O-2	0.039
C-8	−0.032

benzene-ring plane; this implies that the methoxyl group plane bisects the benzene ring. It also means that the C(1) carbon atom is nearly tetrahedral and is coplanar with the rest of the benzene ring. This conformation is recognized to be the least-hindered structure from the steric repulsion of the nitro group. The substituted benzene ring keeps its planarity; the plane can be represented by the equation $0.8250X-0.3683Y+0.4287Z-2.6464=0$. The deviations from this plane for the ring and nitrogen atoms are tabulated in Table 4. The maximum deviation for ring atoms is 0.03 Å at C(2). The bond angles around the C(1) atom are interesting; the C(2)–C(1)–C(6) angle is 108.8° a nearly exact tetrahedral angle, while the O(1)–C(1)–O(2) angle is 100.1°, appreciably smaller than the tetrahedral. The strain produced by this distrotion is significant; it may be explained in terms of the steric repulsion between the methyl groups and the benzene ring, since the C(2)–C(8) and C(6)–C(8) distances are 2.95 Å, both smaller than the sum of the van der Waals radii of two carbon atoms. The bond lengths of C(2)–C(3) and C(5)–C(6) are shorter than those of C(3)–C(4) and C(4)–C(5); this means that the double bonds are localized, as in the structural formula (I) rather than delocalized, as in the structure (II). Of the three nitro groups, the one at the para-position and that at the C(2) ortho-position are tilted 6°30′ and 5°30′ to the benzene ring respectively; the third one, at the C(6) ortho-position, is twisted as much as 11°19′. The crystal structure of 2,4,6-trinitrophenetole, a related parent compound of the nucleophilic substitution reaction, was recently analyzed by Gramaccioli, Destro and Simonetta[10]; it was found that the nitro group at the para position is tilted 3°, the one at the ortho-position is twisted 33°, and the third, at the other ortho-position, is rotated 62°.

Table 4. The deviation of ring atoms from the benzene ring plane

C-1	0.022(Å)
C-2	−0.030
C-3	0.013
C-4	0.011
C-5	−0.020
C-6	0.004
N-1	0.064
N-2	−0.075
N-3	−0.002



(II)

In the present complex three nitro groups are much plainer with the benzene ring than with the trinitrophenetole; this means that the conjugation between the nitro groups and the benzene ring is increased, presumably because an excess electronic charge delocalizes between the nitro groups and the benzene ring. This explanation is also supported by the recent theoretical calculations of Hosoya, Hosoya and Nagakura[11] on this ion. Although the bond lengths of C(1)–C(2) and C(1)–C(6) are slightly different, the present results are not accurate enough for exact discussion. However, these bond lengths are somewhat shorter than the usual single bond length of 1.54 Å; this may be attributed to the hyperconjugation effect of the pseudo π-orbital, composed of two C–O bonds. If we assume that the shortening of the C(1)–C(2)

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10) C. M. Gramaccioli, R. Destro and M. Simonetta, *Chem. Commun.*, **1967**, 331.

11) H. Hosoya, S. Hosoya and S. Nagakura, Preprints for the 21st Annual Meeting of the Chemical Society of Japan (Osaka, 1968).

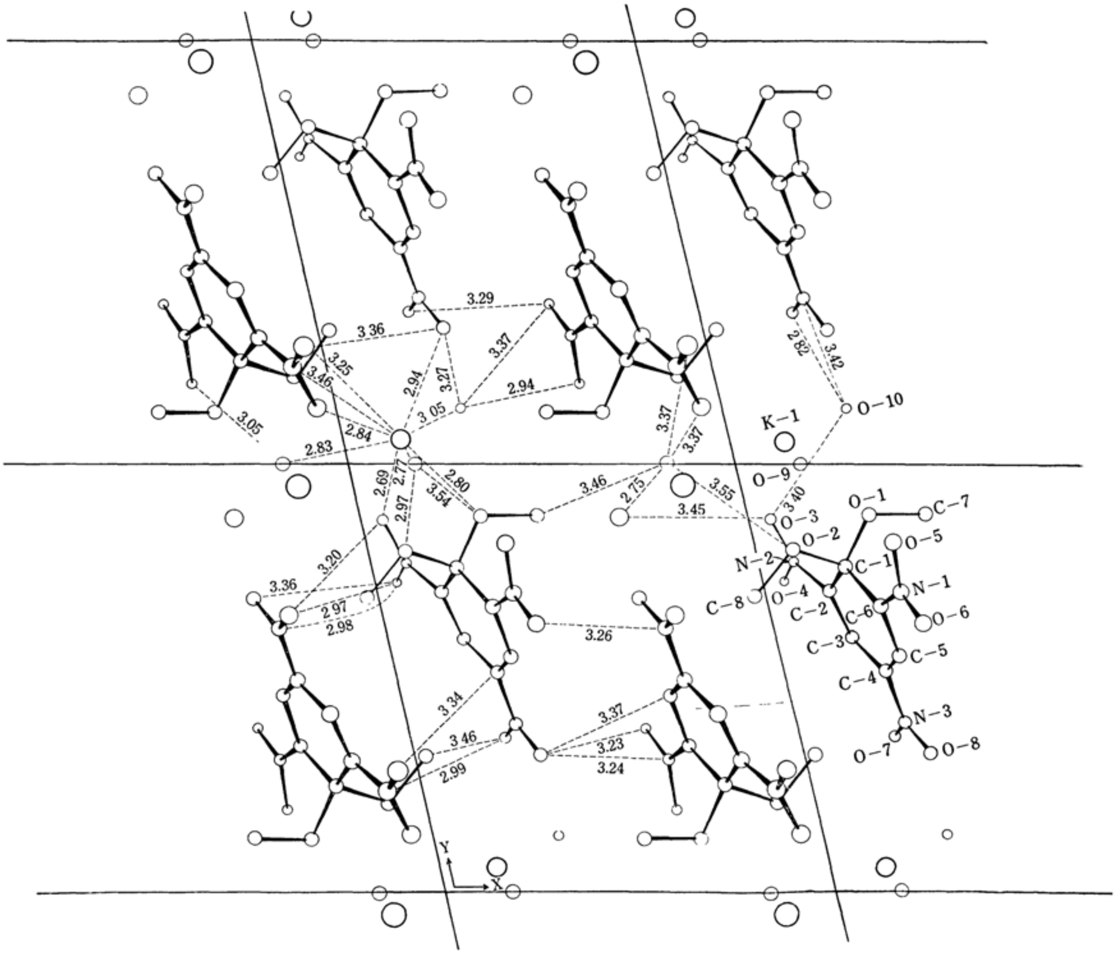

Fig. 3. Interatomic distances between the complex, potassium ion (large and heavy medium circles) and crystalline water (light medium circle and small circles).

or C(1)–C(6) bonds is correlated to the hyperconjugation, it is found that the shorter these bond lengths, the smaller the twisting of the nitro groups at the ortho-positions.

The comparison of the three C–N bond lengths indicates that the shortest one is at the para-position; this is in accord with the structure (I). The distances, C(2)–N(2) and C(6)–N(1), are slightly different from each other, and they are in order on the reverse of that suggested by the magnitude of the conjugation effect. The asymmetry of the Meisenheimer complex with regard to the two ortho nitro groups is unthinkable in a solution. In a crystal, however, the location of the potassium ion is not symmetrical to the three nitro groups. The close distances between the potassium ion and the complex are at two oxygen atoms, (O(3) and 0(8)), of the nitro groups and O(1) and O(2) of the methoxyl groups, as is shown in Fig. 3. The potassium ion in a crystal will attract a negative charge on the neighboring oxygen atoms; as a result, the N–O bond will be lengthened and the nitro group will be more coplanar with the benzene ring. The nitro group at the C(6) ortho position has not potassium ion in the neighborhood; this can explain the largest twisting of this nitro group.

Finally, we should comment on the structure of this complex ion in connection with the mechanism of the nucleophilic substitution reaction. Since Wheland[12] calculated the resonance energy of the activated complex of the substitution reaction, there have been many studies concerning the structure of the reaction intermediate. Two structural formulae, I and II have been proposed, but the structure has not yet been determined accurately. In the present study the complex ion is found to have a quinoid structure of I, and the substituted carbon atom takes a nearly tetrahedral form.

The unusual stability of the reaction intermediate can be explained as resulting from the fact that;

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[12] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(1) the unsaturated five-membered system is stable in the case of the anion; (2) the possibility of hyperconjugation at the tetrahedral carbon atom, and (3) the coplanarity of nitro groups with the benzene ring, which increases the degree of the delocalization of π-electrons.

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