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First Accurate Molecular and Crystal Structure of the *Meisenheimer* Complex of 2,4,6-Trinitrobenzene

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Summary. The first accurate and reliable molecular and crystal structure of the *Meisenheimer* complex of 2,4,6-trinitrobenzene (potassium (1,4-dioxolane)-2-spiro-1′-2′,4′,6′-trinitrocyclohexadienide) has been obtained by X-ray diffraction. The C–NO_2 bond length for the substituent in the para position of the six-membered ring is shorter than for the other ones, and the bond lengths in the unsaturated parts of the anion are not equal. These facts indicate an essential contribution of the 1,4-diene geometry of the ring as well as of the aci resonance forms of the nitro groups to the structure of the anion.

Keywords. Potassium (1,4-dioxolane)-2-spiro-1′,2′,4′,6′-trinitrocyclohexadienide; *Meisenheimer* complex; Molecular structure.

Erste genaue Strukturbestimmung des *Meisenheimer*-Komplexes von 2,4,6-Trinitrobenzol

Zusammenfassung. Die erste genaue und verläßliche Bestimmung der Struktur des *Meisenheimer*-Komplexes von 2,4,6-Trinitrobenzol (Kalium-(1,4-dioxolan)-2-spiro-1′-2′,4′,6′-trinitrocyclohexadienid) gelang mittels Röntgenstrukturanalyse. Die C–NO_2-Bindung des *para*-Substituenten ist länger als die der anderen, und die Bindungslängen in den ungesättigten Domänen des Anions sind unterschiedlich. Diese Tatsachen lassen auf wesentliche Beiträge der 1,4-Dien-Geometrie des Rings und der Aciformen der betreffenden Nitrogruppe zur Struktur des Anions schließen.

Introduction

The formation of *Meisenheimer* or σ-complexes is a key stage of nucleophilic aromatic substitution reactions [1]. Therefore, the molecular structure of *Meisenheimer* complexes, has been of great interest during the last decades [2–5]. A variety of them has been characterized by spectroscopic methods [1, 6].

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However, only a few X-ray diffraction data [7–12] have been obtained due to their instability. On the basis of the crystal data, some features of the molecular structure of such compounds have been determined. In particular, it has been shown that the nitro groups in *Meisenheimer* complexes of 2,4,6-trinitrobenzene derivatives are different. One of them has a shorter C–N bond and longer N–O bonds, indicating a contribution of the aci resonance form to the overall structure. This conclusion agrees well with the absence of full equalization of the endocyclic C–C bonds in the cyclohexadiene ring as derived from spectroscopic data [13].

Unfortunately, all known X-ray diffraction data on *Meisenheimer* complexes of 2,4,6-trinitrobenzene derivatives are of low accuracy, probably caused by the low quality of the single crystals. Therefore, the molecular structural features of the *Meisenheimer* complexes mentioned above should be considered only as trends the differences between the compared geometrical parameters being smaller than the their standard deviations. The low precision of the experimental data is also a very serious problem concerning the estimation of the validity of quantum chemical calculations which are the main sources for information on the molecular structure of such compounds. However, previous theoretical studies have demonstrated some contradiction between the results of calculations using different semi-empirical [2–4] and *ab initio* [5] approaches. For example, investigation of the nucleophilic aromatic substitution reaction between 4-Cl-Ph-CO-SMe and CH_3COO^- by PM3 and DFT methods has indicated the formation of stable *Meisenheimer* complex during the reaction. However, calculations using the HF/6–31 G^{**} method resulted in an opposite conclusion. Due to such contradictory results, the applicability of quantum chemical approaches to such compounds should be examined, *e.g.* by discussing the ability of these methods to describe correctly the geometry of the anions. Unfortunately, so far there are no accurate experimental data.

In the present work we report the first accurate molecular and crystal structure of the *Meisenheimer* complex of 2,4,6-trinitrobenzene (potassium (1,4-dioxolane)-2-spiro-1′–2′,4′,6′-trinitrocyclohexadienide, **1**).

Results and Discussion

In the crystal phase, two molecules of compound **1** (Fig. 1) are solvated by one molecule of 1,4-dioxan. The cyclohexadiene ring in **1** has a boat conformation. The deviations of the C(1) and C(4) atoms from plane of the remaining atoms of the ring are 0.07 Å and 0.04 Å. The C(3)–C(4) and C(4)–C(5) bond lengths (1.388(2) Å and 1.400(3) Å) are close to those of the C_{ar}–C_{ar} bond and much greater than the C(2)–C(3) (1.357(2) Å) and the C(5)–C(6) (1.348(2) Å) distances. Differences in the bond lengths within the conjugated system of the cyclohexadiene ring indicate the absence of full electron density delocalization in this part of the molecule.

The high precision of X-ray experimental data permits to obtain strong structural evidence that the nitro groups in *Meisenheimer* complexes are different. The C(2)–N(1) (1.438(2) Å) and C(6)–N(3) (1.434(2) Å) bond lengths are equal within two standard deviations, whereas the C(4)–N(2) bond (1.418(2) Å) is essentially shorter. The N(2)–O(5) (1.241(2) Å) and N(2)–O(6) (1.240(2) Å) bonds are longer than the N–O bonds in the other nitro groups (N(1)–O(3): 1.231(2) Å,

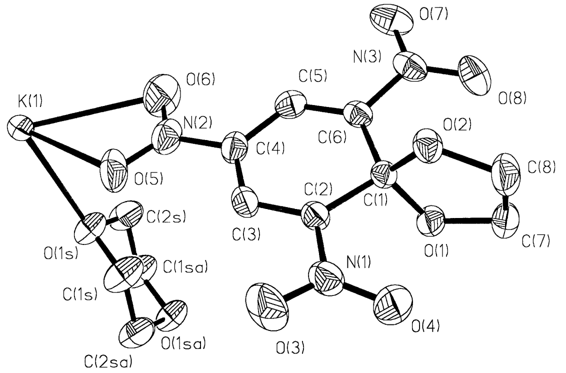

Fig. 1. Molecular structure of compound **1**; thermal ellipsoids are drawn at a 50% probability level; H atoms are omitted for clarity

N(1)–O(4): 1.220(2) Å, N(3)–O(7): 1.228(2) Å, N(3)–O(8): 1.232(2) Å). The observed non-equivalence of the nitro groups together with the bond length distribution in the cyclohexadiene ring indicates a considerable contribution of *aci* resonance forms to the structure of the nitro group in *para* position with respect to the sp^3 carbon atom and of the 1,4-diene form to the structure of the six-membered ring.

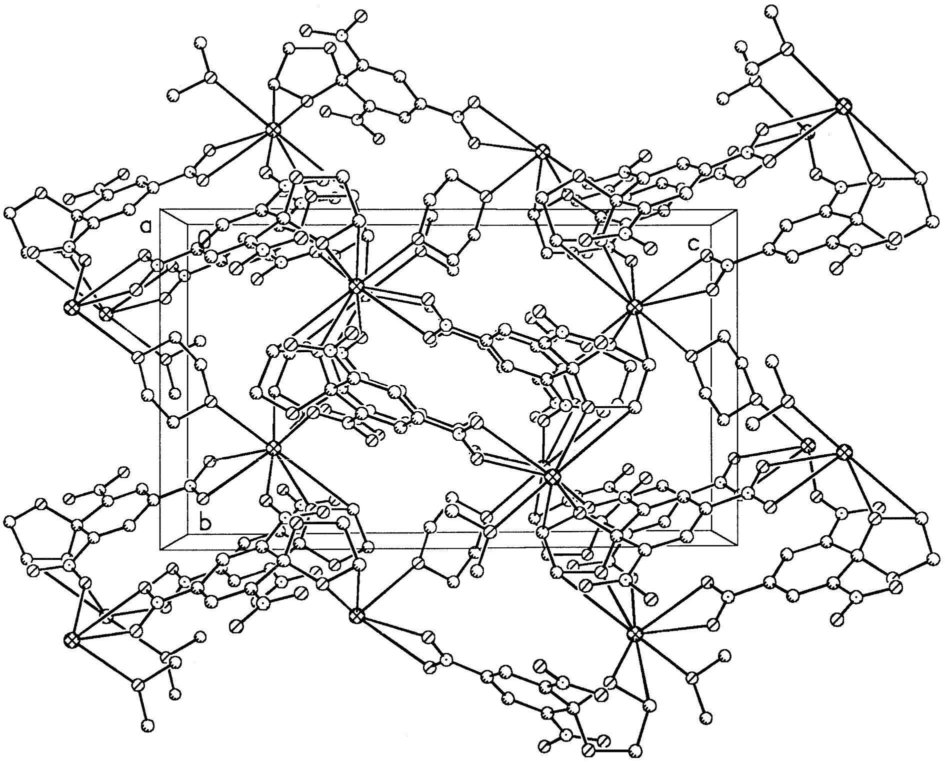

Fig. 2. Crystals packing of compound **1**

The nitro groups at C(4) and C(6) are approximately coplanar to the cyclohexadiene ring (the O(5)–N(2)–C(4)–C(3) and O(7)–N(3)–C(5)–(6) torsion angles are 4.6(3)° and 2.7(2)°, respectively) in spite of the presence of shortened intramolecular contacts: O(8)···C(7) = 2.89 Å (sum of the *van der Waals* radii [16]; 3.00 Å), O(8)···C(8) = 2.89 Å, O(5)···H(3) = 2.41 Å (2.45 Å), O(6)-H(5) = 2.40 Å, and O(7)···H(5) = 2.39 Å. The nitro group at the C(1) atom is twisted with respect to the C(2)–C(3) bond (O(3)–N(1)–C(2)–C(3) torsion angle: −13.8(3)°).

The dioxolane ring has a flattened twist conformation. The deviations of C(7) and O(1) from the plane defined by the remaining atoms of this ring are −0.05 Å

Table 1. Fractional atomic coordinates of non-H atoms (× 10^4) and hydrogen atoms (× 10^3) and equivalent thermal isotropic parameters (Å^2 × 10^3) with e.s.d.s in parentheses for structure **1**

	X	Y	Z	U_{eq}
K(1)	2997(1)	7175(1)	1707(1)	32(1)
O(1)	−178(2)	8994(1)	−2760(1)	35(1)
O(2)	−1413(2)	10834(1)	−2352(1)	33(1)
O(3)	3930(2)	11300(2)	−1670(1)	66(1)
O(4)	2373(2)	10997(2)	−2715(1)	58(1)
O(5)	2810(2)	8743(2)	414(1)	54(1)
O(6)	274(3)	7636(2)	426(1)	66(1)
O(7)	−4606(2)	8107(2)	−1460(1)	56(1)
O(8)	−4103(2)	8978(2)	−2501(1)	52(1)
N(1)	2613(2)	10823(2)	−2047(1)	41(1)
N(2)	1282(3)	8392(2)	113(1)	44(1)
N(3)	−3568(2)	8666(2)	−1864(1)	38(1)
C(1)	−492(2)	9702(2)	−2108(1)	27(1)
C(2)	1339(2)	10022(2)	−1682(1)	29(1)
C(3)	1874(3)	9622(2)	−985(1)	32(1)
C(4)	694(3)	8856(2)	−602(1)	34(1)
C(5)	−1105(3)	8564(2)	−912(1)	33(1)
C(6)	−1682(2)	8966(2)	−1598(1)	29(1)
C(7)	−1039(3)	9600(2)	−3405(1)	47(1)
C(8)	−1748(4)	10841(2)	−3141(1)	47(1)
O(1S)	4470(2)	5680(1)	625(1)	50(1)
C(1S)	5120(4)	6303(2)	−11(1)	58(1)
C(2S)	3577(4)	4531(2)	406(1)	54(1)
H(3)	301(3)	982(2)	−753(1)	49(6)
H(5)	−1834(3)	808(2)	−634(1)	44(6)
H(7B)	−202(4)	905(2)	−360(2)	63(7)
H(7A)	−205(4)	972(2)	−373(2)	63(8)
H(8B)	−110(4)	1155(3)	−333(2)	71(8)
H(8A)	−295(4)	1096(3)	−325(2)	71(8)
H(1SB)	586(3)	703(2)	191(1)	42(6)
H(1SA)	402(5)	647(3)	−402(2)	108(1)
H(2SB)	255(5)	485(3)	92(2)	91(1)
H(2SA)	317(4)	422(3)	855(1)	70(8)

and 0.05 Å, respectively. The angle between the least-squared planes of the six- and five-membered rings is 91.9°.

The crystals of **1** are of polymeric structure (Fig. 2) which is typical for most *Meisenheimer* complexes [7–9, 11, 12]. The potassium atoms form a three-dimensional network due to coordination with oxygen atoms of the nitro groups at C(2) and C(6) (K(1)–O(3)′: 2.731(2) Å, (−x+1, −y+2, −z); K(1)–O(8)′: 2.811(1) Å, (x+1, 1.5−y, z+0.5)) in the first direction, with the oxygen atoms of the 1,4-dioxolane ring (K(1)–O(1)′: 2.811(1) Å, (x, 1.5−y, 0.5+z); K(1)–O(2)′: 2.699(1) Å, (−x, 2−y, −z)) in the second direction, and with the oxygen atoms of solvate molecules of 1,4-dioxan (K(1)–O(1S): 2.778(2) Å) in the third direction. Besides, each potassium atom is coordinated by two oxygen atoms of the nitro group in position 4 of the cyclohexadiene ring (K(1)–O(5): 2.863(2) Å, K(1)–O(6): 2.957(2) Å). Therefore, the coordination of the potassium atom is octahedral.

Accurate determination of the structure of *Meisenheimer* complexes thus confirms the assumption about the non-equivalence of the nitro groups and the absence of full electron density delocalization because of an essential contribution of the 1,4-diene form to the structure of the six-membered ring.

Experimental

Compound **1** was synthesized according to a previously reported procedure [14].

The crystals of $C_8H_6N_3O_8{}^- \cdot K^+ \cdot 0.5C_4H_8O_2$ are monoclinic. At 293 K, $a = 7.137(2)$ Å, $b = 10.618(3)$ Å, $c = 18.048(4)$ Å, $\beta = 93.94(2)°$, $V = 1364.5(5)$ Å^3, space group: P2$_1$/c, $Z = 4$, $D_c = 1.730\,\mathrm{Mg \cdot m^{-3}}$, $\mu = 0.446\,\mathrm{mm^{-1}}$, F(000) = 728. The intensities of 3671 reflections (3382 independent, $R_{int} = 0.022$) were measured on an automatic four-circle Enraf-Nonious CAD-4 diffractometer (graphite monochromated Mo$K\alpha$ radiation, $\theta/2\theta$ scan, $2\theta_{max} = 60°$).

The structure was solved by direct methods using the SHELXTL PLUS 5.02 package [15]. The positions of the hydrogen atoms were located from electron density difference maps. Full-matrix least-squares refinement against F^2 (248 parameters) in anisotropic (isotropic for H-atoms) approximation using 2917 reflections was carried out ($R_1 = 0.031$ (for 2174 reflections with $F > 4\sigma(F)$), $wR_2 = 0.087$, $S = 0.961$). The final atomic coordinates are listed in Table 1. Additional material to the structure determination can be ordered from Fachinformationszentrum Energie-Physik-Mathematik, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany, referring to the deposition no. CSD-59451, the names of the authors, and citation of the paper.

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