Molecular and Crystal Structure of 3,5,5-Trimethyl-2-(2-methyl-2-nitropropyl)-2-cyclohexen-1-one Possessing Molecular Asymmetry

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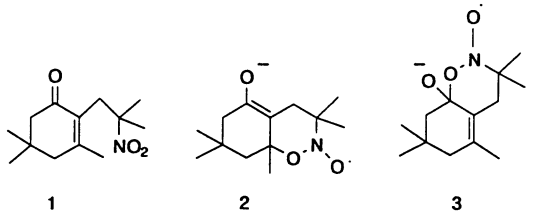
Synopsis. The crystal structure of an aliphatic nitro compound with atropisomerism, $C_{13}H_{21}NO_3$, has been determined by X-ray diffraction at ambient temperature. The monoclinic structure ($P2_1/c$, Z=8) was refined by the full-matrix least-squares method to a final R=0.040 for 2394 observed unique reflections. Two crystallographically independent molecules consist of a pair of atropisomers. The intramolecular O···H–C type hydrogen bonds (O···C(methyl): 3.21—3.54 Å) and the contact between the nitro oxygen and ethylenic carbon atoms (O···C: 3.24 and 3.36 Å) may be responsible for this isomerism.

Recently we have observed a novel nitroxide radical species by ESR as an actual reaction intermediate in the reaction of $LiC(CH_3)_2NO_2$ with 3,5,5-trimethyl-2-(phenylsulfonylmethyl)-2-cyclohexen-1-one affording 3,5,5-trimethyl-2-(2-methyl-2-nitropropyl)-2-cyclohexen-1-one **1**.[1] The molecular structure of this radical has not been assigned by the ESR studies, because of no exhibition of hyperfine structure due to any other magnetic nucleus than nitrogen one. Since the identical radical species has been detected during photoirradiation of a *N,N*-dimethylformamide (DMF) solution of **1** alone, we concluded that the structure of the observed radical species must be very close to that of **1** and proposed it as the nitroxide radical anion **2** or **3**. Therefore, we have considered that the elucidation of the molecular structure of **1** may offer useful information on which structure of **2** or **3** is more plausible, and have performed an X-ray diffraction study for **1**.



1 2 3

Experimental

Material Preparation. To $LiC(CH_3)_2NO_2$ (7.0 mmol) in DMF (15 ml) under argon atmosphere was added a DMF (10 ml) solution of 3,5,5-trimethyl-2-(phenylsulfonylmethyl)-2-cyclohexen-1-one (5.0 mmol). The reaction mixture was stirred at room temperature for 48 h. Then it was partitioned between ether (50 ml) and water (50 ml), and the aqueous phase was extracted with ether (3×30 ml). The ether extract was washed with brine (3×30 ml) and water (30 ml), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography (20/1 hexane/ethyl acetate); **1**: mp 318—320 K. Single crystals suitable for the diffraction were hardly obtained by recrystallization from polar solvents, because of its high solubility. The colorless crystal used in this study was obtained by recrystallization from heptane solution in a capped tube by very slow evaporation of the solvent at ambient temperature.

Structure Determination. The most suitable crystal (rather spheroidal; 0.37×0.37×0.23 mm³) coated with collodion was mounted on an automated four-circle diffractometer, Rigaku AFC5R, equipped with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å). The cell dimensions were obtained using 25 reflections ($45.4<2\theta<52.3°$). By using the ω–2θ scan mode with a scan rate 16° min^{-1} (in ω), intensities of 3660

Table 1. Final Atomic Coordinates (×10⁴) and Their Equivalent Isotropic Temperature Factor,[a] with esd's (in Parentheses)

Atom	x	y	z	B_{eq}[b]/Å²
O(1)	3841(1)	4539(2)	1506(2)	5.2(1)
O(2)	3804(1)	4380(3)	5736(2)	7.3(1)
O(3)	3010(1)	4008(3)	5615(2)	8.0(2)
N(1)	3393(1)	3902(3)	5221(2)	4.9(1)
C(1)	3869(1)	5587(3)	2199(2)	3.3(1)
C(2)	3513(1)	5727(3)	3024(2)	2.9(1)
C(3)	3501(1)	7013(3)	3616(2)	3.1(1)
C(4)	3884(1)	8231(3)	3607(2)	3.3(1)
C(5)	4385(1)	7727(3)	3311(2)	3.2(1)
C(6)	4243(1)	6817(3)	2166(2)	3.6(1)
C(7)	3162(1)	4418(3)	3057(2)	3.6(1)
C(8)	3356(1)	3190(3)	3980(2)	3.6(1)
C(9)	3876(1)	2597(3)	3916(3)	4.9(2)
C(10)	2969(1)	1941(4)	3871(3)	5.5(2)
C(11)	3099(1)	7377(5)	4316(4)	5.0(2)
C(12)	4692(1)	6778(3)	4323(2)	4.2(1)
C(13)	4705(1)	9067(3)	3119(3)	4.8(1)
O(11)	8832(1)	4519(2)	2354(2)	5.3(1)
O(12)	8854(1)	4336(3)	−1847(2)	6.1(1)
O(13)	8066(1)	3981(3)	−2596(2)	6.7(1)
N(11)	8439(1)	3868(3)	−1777(2)	4.1(1)
C(21)	8863(1)	5559(3)	1681(2)	3.5(1)
C(22)	8512(1)	5699(3)	498(2)	3.0(1)
C(23)	8502(1)	6986(3)	−110(2)	3.1(1)
C(24)	8884(1)	8208(3)	290(2)	3.4(1)
C(25)	9386(1)	7694(3)	1081(2)	3.1(1)
C(26)	9244(1)	6784(3)	2085(2)	3.6(1)
C(27)	8161(1)	4396(3)	105(2)	3.7(1)
C(28)	8371(1)	3153(3)	−599(2)	3.4(1)
C(29)	8881(1)	2546(3)	32(3)	4.5(1)
C(30)	7979(1)	1918(4)	−915(3)	5.6(2)
C(31)	8109(1)	7352(5)	−1210(4)	4.7(2)
C(32)	9691(1)	6743(3)	373(2)	4.0(1)
C(33)	9708(1)	9030(3)	1599(3)	4.6(1)

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

unique reflections were measured up to 110° in 2θ. The scan width was $\Delta\omega=(1.37+0.30\tan\theta)°$. Corrections were made for the Lorentz and polarization factors.

Crystal Data: $C_{13}H_{21}NO_3$, $M_r=239.31$; monoclinic, space group $P2_1/c$; $a=26.797(2)$, $b=8.992(1)$, $c=11.398(2)$ Å; $\beta=102.11(1)°$; $V=2685(1)$ Å^3; $Z=8$; $D_c=1.184$ g cm^{-3}; $F(000)=1040$; μ(Cu $K\alpha$)=6.41 cm^{-1}.

Three standard reflections monitored at every 150 reflections showed intensity deterioration down to 75% of initial ones. The falling-off of intensities with the elapse of time was corrected based on the linear decay in the standard reflections. The similar falling-off was observed for certain nitramines during their radiolysis by X-ray.[2] An empirical correction for the absorption was made based on azimuthal (Ψ) scans of three reflections.[3] The structure was solved by the direct method using MITHRIL program.[4] The coordinates and anisotropic thermal parameters for the non-hydrogen atoms and coordinates and isotropic thermal parameters of 3-methyl hydrogen atoms were refined by the full-matrix least-squares procedure based on F with weight $w=1/\sigma^2(F)$. The positions of the other hydrogen atoms were calculated from those of the non-hydrogen atoms and were included in F_c calculation. Calculations were carried out on a VAX station 3200 computer with TEXSAN programs[5] which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography"[6] and took anomalous dispersion into account. The final refinement yield $R=0.040$, $R_w=0.048$, and goodness-of-fit=1.64 for 2394 observed independent reflections ($I>3.0\sigma(I)$) and 332 variables including secondary extinction coefficient. The final atomic parameters for the non-hydrogen atoms are given in Table 1.[7]

Results and Discussion

There are two crystallographically independent molecules consisting of a pair of atropisomers. All the corresponding bond distances and angles of the two molecules are in good accordance with each other within 3σ, except for C(8)–N(1)–O(2) angle which differs by 5σ. Figure 1 shows a molecular perspective view with atom labeling scheme.

The atoms C(1), C(3), C(4), and C(6) are coplanar within 0.01 Å deviation, but C(2) and C(5) are deviated by 0.08 and 0.65 Å from this plane, which takes an distorted boat form. The dihedral angle between the planes defined by C(2)–C(1)–C(6) and C(2)–C(3)–C(4) is 172°.

The pertinent data on the molecular geometry are listed in Tables 2 and 3. The C(8)–N(1) bond distance of 1.54 Å is longer than those of other aliphatic nitro compounds (1.475 Å,[8] 1.46—1.50 Å[9]). This is probably due to the non-bonding O(2)···C(9) contact (2.66 Å).

Intramolecular O(1)···C(9) and O(3)···C(11) contacts are 3.24 and 3.40 Å, respectively, which are significantly

Table 2. Selected Bond Distances (l/Å)

	Molecule A	Molecule B
O(1)–C(1)	1.223(3)	1.224(3)
C(1)–C(2)	1.478(3)	1.478(4)
C(2)–C(3)	1.343(3)	1.346(3)
C(1)–C(6)	1.498(4)	1.507(4)
C(3)–C(4)	1.503(4)	1.506(4)
C(2)–C(7)	1.512(4)	1.510(4)
C(3)–C(11)	1.504(4)	1.495(4)
C(8)–N(1)	1.537(4)	1.534(3)
N(1)–O(2)	1.214(3)	1.207(3)
N(1)–O(3)	1.205(3)	1.220(3)
C(8)–C(7)	1.538(4)	1.548(4)
C(8)–C(9)	1.508(4)	1.509(4)
C(8)–C(10)	1.517(4)	1.518(4)

Table 3. Pertinent Intramolecular Separations (l/Å)

Atom 1	Atom 2	Molecule A	Molecule B
O(1)	C(9)	3.240(4)	3.212(4)
C(9)	O(2)	2.660(4)	2.668(4)
O(2)	C(11)	3.489(5)	3.533(5)
C(10)	O(3)	2.707(4)	2.712(4)
O(3)	C(11)	3.402(5)	3.409(5)
O(1)	H(7)	3.00	2.94
O(1)	H(9)	2.84	2.84
O(3)	H(1B)	2.91(4)	2.89(4)
O(2)	C(3)	3.359(4)	3.358(3)
O(2)	C(2)	3.259(3)	3.243(3)

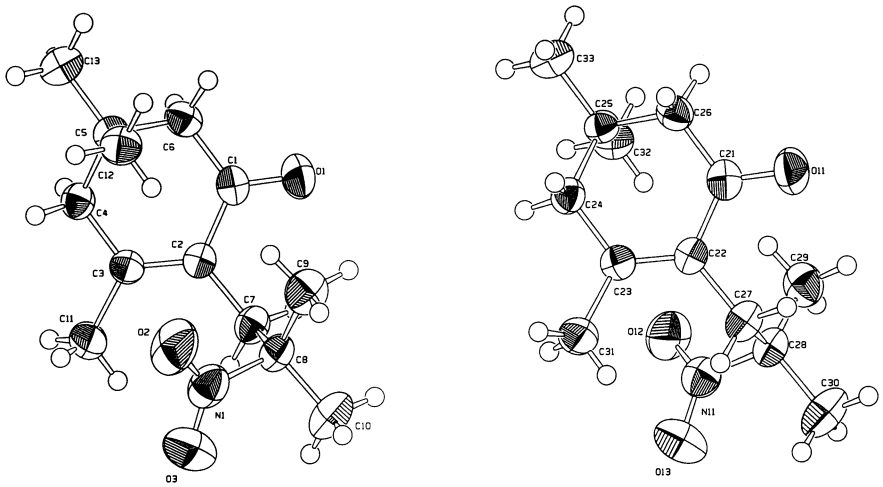


Fig. 1. Perspective view of a pair of atropisomer of the title compound. Open circles represent hydrogen atoms. Ellipsoids have been drawn at 50% probability.

shorter than the sum of the van der Waals radii (1.52+2.0=3.52 Å[10]) between an oxygen atom and a methyl group. Actually, 3.50 Å is the shortest intermolecular O···C(methyl) contact in this crystal. The aforementioned intramolecular contacts (O(1)···O(9) and O(3)···C(11)) imply hydrogen bonding of O···H–C type, taking account into the highly polarized nature of the N–O and C=O bonds.[11] This interaction is certainly responsible for the atropisomerism of this compound in crystalline state. In view of the ordinary thickness (3.5 Å) of a π-bonded system, O(2)···C(2) and O(2)···C(3) contacts (3.26 and 3.36 Å), respectively, suggest possibility of the π-bonding interaction. Molecular orbital calculations (AM1[12]), however, indicated that the π-bonding interaction probably did not play a dominant role. This molecular structure of **1** suggests that the enolate form of **2** is more plausible than **3** for the radical species generated by the photoirradiation on **1**.

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