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6-NITROBENZONORBORNEN-2-ONE

$C_{11}H_9NO_3$

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Preliminary Information. The known (Tanida, Irie and Tsushima, 1970) title compound was prepared both as a model compound and as a precursor for other model compounds (NH_2, I) for a ^{13}C NMR study of aromatic ring-substituted benzonorbornenes. Since an unambiguous assignment of the site of attachment of the nitro group was essential, an X-ray structure determination was performed on the title compound (recrystallized from methanol).

Crystal Data. Single-crystal diffractometry, graphite monochromated MoKα λ=0.7107Å, space group $P\bar{1}$, a=6.251(1), b=9.208(3), c=9.389(2)Å, α=95.60°(2), β=108.37°(2), γ=109.58°(2), Z=2, d_{calc}=1.43, d_{obs}=1.40g/cm^3.

Intensity Data, Structure Determination and Refinement. Intensity data were collected on a Syntex $P2_1$ diffractometer using a θ-2θ scan procedure in the range of $4°<2\theta<60°$. 1839 of the reflections with $I>3\sigma(I)$ were used in the analysis. The structure was solved by direct methods using the MULTAN 78 computer system (Main, Hull, Lessinger, Germain, Declercq and Woolfson, 1978). The refinement was carried out by the full matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located from a difference electron density map and included in the refinement with fixed isotropic temperature factors. The final discrepancy factors are $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|=0.046$ and $R'=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}=0.050$. Structure factor data and anisotropic temperature factors are available upon request from the authors.

Atomic Coordinates ($\times 10^4$)

	x/a(σ)	y/b(σ)	z/c(σ)
C1	5618(3)	8237(2)	6843(2)
C2	3444(3)	8114(2)	5445(2)
C3	1451(3)	8122(2)	6045(2)
C4	2632(3)	8149(2)	7768(2)
C5	1799(3)	5276(2)	8303(2)
C6	2505(3)	4007(2)	8141(2)
C7	4244(3)	4004(2)	7538(2)
C8	5397(3)	5341(2)	7063(2)
C9	5294(4)	9254(2)	8102(2)
C4a	2946(3)	6590(2)	7830(2)
C8a	4759(3)	6626(2)	7232(2)
N	1323(3)	2593(2)	8658(2)
O1	171(3)	2704(2)	9466(2)
O2	1562(3)	1372(1)	8247(2)
O3	3307(2)	8020(1)	4125(1)

Bond Lengths (Å)

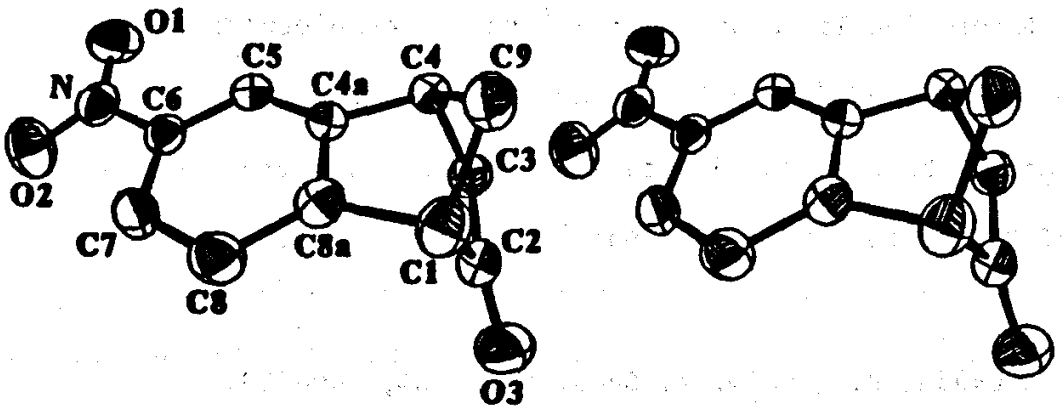
C1-C2	1.525(2)
C1-C8a	1.523(2)
C1-C9	1.542(3)
C2-C3	1.522(2)
C2-O3	1.207(2)
C3-C4	1.546(2)
C4-C4a	1.516(2)
C4-C9	1.542(2)
C4a-C5	1.378(2)
C4a-C8a	1.407(2)
C5-C6	1.392(2)
C6-C7	1.376(2)
C6-N	1.477(2)
C7-C8	1.396(2)
C8-C8a	1.379(2)
N-O1	1.218(2)
N-O2	1.224(2)

Hydrogen Atomic Coordinates ($\times 10^3$)

	x/a(σ)	y/b(σ)	z/c(σ)
H(C1)	711(3)	858(2)	668(2)
H1(C3)	-3(3)	718(2)	548(2)
H2(C3)	114(3)	911(2)	591(1)
H(C4)	184(3)	845(2)	840(2)
H(C5)	64(3)	525(2)	873(2)
H(C7)	472(3)	314(2)	748(2)
H(C8)	657(3)	533(2)	666(2)
H1(C9)	640(3)	932(2)	913(2)
H2(C9)	544(3)	1031(2)	791(2)

Bond Angles(°)

C2-C1-C8a	103.2(1)
C2-C1-C9	100.0(1)
C8a-C1-C9	100.3(1)
C1-C2-C3	106.1(1)
C1-C2-O3	127.4(1)
C3-C2-O3	126.5(1)
C2-C3-C4	102.3(1)
C3-C4-C4a	106.6(1)
C3-C4-C9	100.0(1)
C4a-C4-C9	99.7(1)
C4-C4a-C8a	106.9(1)
C5-C4a-C8a	120.6(1)
C4a-C5-C6	116.8(1)
C5-C6-C7	123.6(1)
C6-C7-C8	119.1(2)
C7-C8-C8a	118.5(2)
C1-C8a-C4a	106.3(1)
C8-C8a-C4a	121.4(1)
C1-C9-C4	95.1(1)
O1-N-O2	123.7(1)
C6-N-O1	118.4(1)
C6-N-O2	117.9(1)



STEREO VIEW OF THE TITLE COMPOUND. Atom labeling scheme used same as in tables. Hydrogen atoms omitted for clarity.

Comments. (i) The site of attachment of the nitro group is established. (ii) Bond angles suggest the presence of considerable strain in the norbornenone nucleus; the C1-C9-C4 bridging angle is 95.1°, the C1-C2-C3 angle at the carbonyl is 106.1° and the endocyclic angles at the double bond are only 106.3° and 106.9°. (iii) Bond lengths and angles are similar to those reported for the benzonorbornene nuclei (Koyama and Okada, 1969 and Sato, Shiro and Koyama, 1968). (iv) C1 and C4 deviate from the mean plane of the benzene ring by only 0.06 and -0.01Å respectively. (v) The dihedral angle between the mean planes C1-C2-C3-C4 and C4-C4a-C8a-C1 is 110.6° with the C9 bridging carbon tilted away from the benzene ring (dihedral angles of the C1-C9-C4 plane with the C1-C2-C3-C4 and C4-C4a-C8a-C1 mean planes are 122.8° and 126.5°, respectively). (vi) The dihedral angle between the plane of the nitro group and the mean plane of the benzene ring is 14.5° due to a twist about the C6-N bond. (vii) There are no close intermolecular distances; all the intermolecular contacts correspond to normal van der Waals forces.

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References

Koyama, H. and Okada, K. (1969), J. Chem. Soc. (B), 940-950.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. and Woolfson, M. M., (1978), "MULTAN 78: A Computer Program for the Automatic Solution of Crystal Structures", Department of Physics, University of York, York, England.

Sato, T., Shiro, M. and Koyama, H. (1968), J. Chem. Soc. (B), 935-944.

Tanida, H., Irie, T. and Tsushima, T., (1970), J. Amer. Chem. Soc., 92, 3404-3409.

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