

Conformations of 1,2-Dicyano-1,1,2,2-tetraphenylethane and Cyanodiphenylmethyl Peroxide

Yulin Lam,* Gene-Hsiang Lee,[†] and Eping Liang

Department of Chemistry, National University of Singapore,
3 Science Drive 3, Singapore 117543

[†]Instrumentation Centre, National Taiwan University, Taipei
10764, Taiwan

(Received October 24, 2000)

The solid-state structures of 1,2-dicyano-1,1,2,2-tetraphenylethane and cyanodiphenylmethyl peroxide are determined by X-ray crystallography. Both molecules adopt the *trans* conformation in the solid-state. Experimentally derived values of the energy difference between the *gauche* and *trans* rotamers and their population quotient are compared with values predicted by semiempirical MO calculations.

Earlier works on the dicyano series of compounds have shown contrasting results, with 1,2-dicyanoethane¹ and 9,9'-dicyano-9,9'-bifluorenyl² existing predominantly in the *gauche* form, whilst other dicyano compounds containing phenyl and alkyl substituents generally favor the *trans* conformation.^{3,4} Through the years, various studies on 1,2-dicyano-1,1,2,2-tetraphenylethane **1** have been carried out^{5–7} but no experimental evidence has been published which would bear directly on the conformational preference of the molecule in the solid-state. We now report our findings on **1** and its peroxide analogue, cyanodiphenylmethyl peroxide **2**, based on X-ray diffraction measurements and semiempirical molecular orbital calculations.

Figure 1 depicts the structures and defines the atomic numbering of **1** and **2**. The pair of central carbon atoms of molecule **1** is slightly disordered and occupies two possible sites, C(1) and C(1') and C(2) and C(2'), as shown in Fig. 1a), with occupancy factors of 0.805(16):0.195(16). Since there is finite movement of these central carbon atoms, the bond lengths, bond angles and torsion angles involving them are consequently not physically significant.

Projection down the C(1)–C(2) bond clearly shows that **1** adopts a *trans* conformation, like meso-2,3-dicyano-2,3-diphenylbutane³ and 1,1,2,2-tetraphenylethane,⁸ but in contrast with its back-clamped analogue, 9,9'-dicyano-9,9'-bifluorenyl,² which exists in the solid-state as a *gauche* structure with a CN–C–C–CN torsion angle of ~56.5°. This difference in conformational behavior between **1** and 9,9'-dicyano-9,9'-bifluorenyl confirms the manifestation of the effects of phenyl ring stacking in **1**; it is consistent with theory that there is a tendency for neighboring phenyl rings in an unclamped polyarylethane to nest or stack so as to diminish the geminal repulsions

and the valence angle spread.⁸

Earlier studies⁵ on the conformation of **1** show that the molecule exists almost entirely in the *trans*-configuration in the solution-state with a ΔE value of 13.39–14.23 kJ mol^{–1}. Since no computational results exist which would represent the conformational preference of **1** in the gaseous state, we therefore subjected our experimental conclusions to a computational test. AMPAC calculations with AM1 parametrization and full geometry optimization clearly showed that the *trans* rotamer has a lower energy than the *gauche* form, differing from it by 10.66 kJ mol^{–1}. The torsion angle of the *gauche* rotamer with the lowest energy was found to be 62° and the Boltzmann distribution to be 97.4% *trans* and 2.6% *gauche*. These data compare well with the results obtained in both solid- and solution-state experiments.

Molecule **2** adopts a *trans* conformation. The presence of a peroxide group appears to relieve some of the strong interactions between the phenyl moieties. The phenyl groups are arranged in a propeller-like conformation, with rings A and B be-

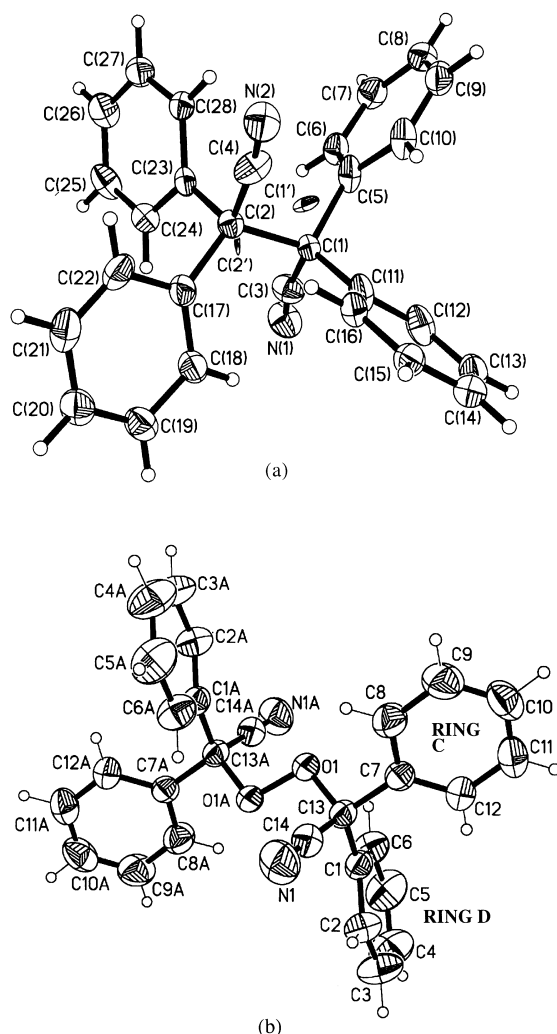


Fig. 1. (a) Thermal ellipsoid diagrams of **1** at 30% probability. (b) Thermal ellipsoid diagrams of **2** at 30% probability

ing oriented at $38.63(17)^\circ$ and $51.87(16)^\circ$ to the C(1)–C(13)–O(1) and C(7)–C(13)–O(1) planes respectively.

AMPAC calculations of **2** show that the *trans* isomer with a C–O–C torsion angle of 134° and the phenyl rings oriented at 21.9° and 44.31° to the respective C(sp²)–C(sp³)–O plane is the preferred structure. These results are in broad agreement with our experimental values.

Experimental

Preparation of 1 and 2. To diphenylacetonitrile (2.90 g, 15 mmol) was added *t*-butyl peroxide (1.30 g, 8.9 mmol) and the reaction was gently refluxed for 2 days. On cooling, solid was deposited in the yellow solution. The solution was decanted and the solid washed thoroughly with hot methanol and then fractionally recrystallized from benzene to give **1** (1.96 g, 5.1 mmol) and **2** (0.51 g, 1.2 mmol). Compound **1** is a white solid, mp $214\text{--}215^\circ\text{C}$ (decomp) (from benzene) (Ref. 9, $213\text{--}215^\circ\text{C}$). Anal. Calcd for C₂₈H₂₀N₂: C, 87.45; H, 5.25; N, 7.30%; *M_r*, 384. Found: C, 87.42; H, 5.33; N, 7.25%; *M⁺*, 384.2. Compound **2** is a white solid, mp 191°C (from benzene). Anal. Calcd from C₂₈H₂₀N₂O₂: C, 80.77; H, 4.81; N, 6.73%; *M_r*, 416. Found: C, 80.75; H, 4.78; N, 6.80%; *M⁺*, 416.

X-ray Crystallography. Colorless crystals of **1** and **2** were obtained from benzene–hexane mixtures. Crystallization of **1** proved extremely difficult because the crystals were often poorly formed. In an attempt to obtain crystals more suitable for the determination of the crystal structure, a saturated solution of **1** in benzene–hexane was allowed to slowly evaporate at 5°C .

Data collection of **1** was performed at 295 K on a NONIUS CAD4 diffractometer using graphite-monochromated Mo-*K*α radiation ($\lambda = 0.71073\text{ \AA}$) whilst data collection of **2** was performed at 298 K using a Siemens R3m/V200 diffractometer with graphite-monochromated Mo-*K*α radiation ($\lambda = 0.71073\text{ \AA}$). Both structures were solved using the direct method and refined by full-matrix least squares on *F*² values using the programs of SHELXL-Plus.¹⁰ Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were treated as riding on their attached atoms and refined isotropically. Crystal data for **1**: C₂₈H₂₀N₂, *M_r* = 384.46, monoclinic, space group *P*2₁/*n*, *a* = $9.390(2)$, *b* = $16.118(3)$, *c* = $13.598(3)\text{ \AA}$, $\beta = 90.53(2)^\circ$, *V* = $2057.9(7)\text{ \AA}^3$, *Z* = 4, *D*_{calc} = 1.241 g cm^{-3} , $\mu = 0.073\text{ mm}^{-1}$, crystal size $0.60 \times 0.20 \times 0.04\text{ mm}$, 3624 reflections measured ($2\theta = 50.0^\circ$), 3624 independent reflections [*I* > 2σ(*I*)] used in the refinement; *R* = 0.0795, *R_w* = 0.2148 and GOF = 1.102 for 290 parameters. Crystal data for **2**: C₂₈H₂₀N₂O₂, *M_r* = 416.46, monoclinic, space group

*C*2/*c*, *a* = $17.310(7)$, *b* = $7.7679(16)$, *c* = $17.650(6)\text{ \AA}$, $\beta = 106.561(16)^\circ$, *V* = $2274.9(13)\text{ \AA}^3$, *Z* = 4, *D*_{calc} = 1.216 g cm^{-3} , $\mu = 0.077\text{ mm}^{-1}$, crystal size $0.40 \times 0.40 \times 0.36\text{ mm}$, 6921 reflections measured ($2\theta = 58.3^\circ$), 2824 independent reflections [*I* > 2σ(*I*)] used in the refinement; *R* = 0.0511, *R_w* = 0.1161 and GOF = 1.093 for 185 parameters. Lists of final atomic coordinates, bond lengths and angles, thermal parameters and torsion angles have been deposited as Document No. 14030 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

Calculations. Semiempirical molecular orbital calculations were performed using the program¹¹ AMPAC 6.51 with AM1 parametrization.¹² Structural parameters were taken from our X-ray diffraction results of the compounds. Full geometry optimization was performed for each incremental value of the torsion angle which were defined by the atoms CN–C–C–CN in **1** and C–O–O–C in **2** according to the convention of Klyne and Prelog.¹³

References

- 1 R. J. W. LeFèvre, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc. B*, **1967**, 819.
- 2 Y. L. Lam, L. L. Koh, H. H. Huang, and L. Wang, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1137.
- 3 Y. L. Lam, L. L. Koh, and H. H. Huang, *J. Chem. Res. (M)*, **1991**, 2119; *J. Chem. Res. (S)*, **1991**, 212.
- 4 L. H. L. Chia, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc. B*, **1969**, 608.
- 5 K. K. Chui, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc.*, **1970**, 304.
- 6 J. Plaček and F. Szöcs, *Macromol. Chem. Phys.*, **195**, 463 (1994).
- 7 A. Bledzki, D. Braun, F. Szöcs, and J. Plaček, *Macromol. Chem., Rapid Commun.*, **6**, 649 (1985).
- 8 D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977).
- 9 K. K. Chui and H. H. Huang, *J. Chem. Soc. C*, **1969**, 2758.
- 10 Siemens, SHELXTL-PLUS, Release 4.20, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1990).
- 11 M. J. S. Dewar, J. J. P. Stewart, J. M. Ruiz, D. Liotard, E. F. Kealy, and R. D. Dennington II, AMPAC 6.5, Semichem Inc., USA (1997).
- 12 M. J. S. Dewar, E. G. Zoebisch, E. F. Healey, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
- 13 W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).