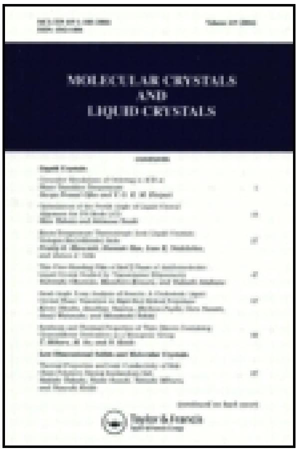


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

On the Conformational Analysis and Photochemical Reactivity of 1,6-Cyclodecanedione

Thillairaj J. Lewis [a], Steven J. Rettig [a], Ronald R. Sauers [b], John R. Scheffer [a], James Trotter [a] & Chung-Hsi Wu [a]

[a] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, Canada, V6T 1Z1

[b] Department of Chemistry, Rutgers University, P.O. Box 939, Piscataway, NJ, 08855-0939

To cite this article: Thillairaj J. Lewis, Steven J. Rettig, Ronald R. Sauers, John R. Scheffer, James Trotter & Chung-Hsi Wu (1996): On the Conformational Analysis and Photochemical Reactivity of 1,6-Cyclodecanedione, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 289-298

To link to this article: http://dx.doi.org/10.1080/10587259608046034

Mol. Cryst. Liq. Cryst., 1996, Vol. 277, pp. 289–298
Reprints available directly from the publisher
Photocopying permitted by license only

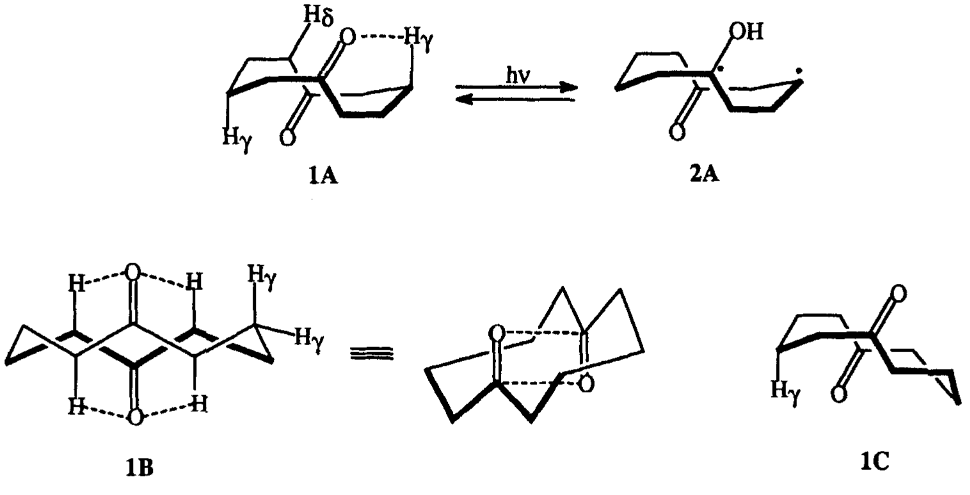
ON THE CONFORMATIONAL ANALYSIS AND PHOTOCHEMICAL REACTIVITY OF 1,6-CYCLODECANEDIONE

THILLAIRAJ J. LEWIS,[†] STEVEN J. RETTIG,[†] RONALD R. SAUERS,[‡] JOHN R. SCHEFFER,[*†] JAMES TROTTER[†] and CHUNG-HSI WU[†]
[†]Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, Canada V6T 1Z1 and [‡]Department of Chemistry, Rutgers University, P.O. Box 939, Piscataway, NJ 08855-0939

Abstract Photolysis of 1,6-cyclodecanedione, both in the crystalline state and in solution, fails to lead to any Norrish/Yang type II products despite the fact that the conformation of the molecule in the solid state is nearly ideal for hydrogen atom abstraction. Based on X-ray crystal structure and molecular modeling studies, it is argued that γ-hydrogen abstraction does occur in the solid state, but that closure of the resulting 1,4-biradical is slower than reverse hydrogen atom transfer owing to difficulty in forming the expected 8-membered ring-containing photoproduct. In solution, on the other hand, molecular mechanics calculations indicate that the lack of photoreactivity of 1,6-cyclodecanedione stems from the fact that this molecule exists nearly exclusively in a conformation for which γ-hydrogen abstraction is sterically impossible.

As part of a systematic study of the solid state and solution phase photochemistry of macrocyclic and medium-sized ring "diametric" diketones,[1,2,3] we recently turned our attention to 1,6-cyclodecanedione (**1**). Based on the literature reports of the photochemistry of cyclodecanone[4,5] and 1,2-cyclodecanedione,[6] we expected that 1,6-cyclodecanedione would undergo photoinduced γ-hydrogen abstraction and subsequent cyclobutanol formation (Yang cyclization), and we were therefore surprised to discover that irradiation of this diketone under a variety of conditions led to no significant accumulation of photoproducts. We report here the results of our efforts to understand this unusual behavior.

1,6-Cyclodecanedione was prepared by ozonolysis of 1,2,3,4 5,6,7,8-octahydronaphthalene according to the procedure of Hückel et al.[7] Prolonged photolysis of this material through Pyrex at room temperature in hexane, *tert*-butanol or the crystalline state led to no significant buildup of products detectable by TLC or GC. The crystal structure of 1,6-cyclodecanedione shows that it adopts the boat-chair-boat conformation **1A** in the solid state (Scheme 1).[8] This conformation is common to most other cyclodecane derivatives whose crystal structures have been determined.[9] Conformer **1A** is ideally arranged for abstraction of the indicated γ-hydrogen (dotted lines), with values of **d** (the C=O...H_γ distance), ω (the degree to which H_γ lies outside the mean plane of the carbonyl group), Δ (the C=O...H_γ angle) and θ (the C-H_γ...O angle) of 2.74 Å, 52°, 91° and 113°, respectively. These parameters are essentially identical to those of ketones that *do* react photochemically in the solid state.[1-3,10] The other set of γ-hydrogen atoms in conformer **1A** has **d** > 3.50 Å, a distance too great for abstraction.



SCHEME 1 1,6-Cyclodecanedione Conformations

A second indication that H_γ in conformer **1A** should be readily abstracted comes from a theoretical analysis of the process according to recently developed molecular mechanics[5,11] and semiempirical[12] procedures - calculations that have been used successfully to model a wide variety of Norrish/Yang type II photoreactions. In these methods, the difference in energy between the triplet excited state of a ketone and its hydrogen atom abstraction transition state is estimated computationally using MM2-based or MINDO/3 methodology, and the results indicate that when the difference in steric energy (Δ SE) exceeds approximately 5 kcal/mole (MM2), or when the activation enthalpy ($\Delta H^\ddagger$) is greater than *ca.* 19 kcal/mole (MINDO/3), abstraction is not observed. Previous work has shown that the successful γ-hydrogen abstraction reaction of cyclodecanone in its boat-chair-boat conformation is associated with a Δ SE value of 2.8-3.0 kcal/mole (MM2)[5] and that $\Delta H^\ddagger$ = 13.1 kcal/mole (MINDO/3).[12] Application of these methods in the present instance to conformer **1A** of 1,6-cyclodecanedione indicates that the increase in steric energy (Δ SE) accompanying γ-hydrogen abstraction is 2.1-2.3 kcal/mole (MM2) and $\Delta H^\ddagger$ = 12.3 kcal/mole (MINDO/3) - both significantly *less* than for cyclodecanone and well within the limits set for other type II reactive alkanones.[13]

It thus seems likely that 1,6-cyclodecanedione *does* undergo γ-hydrogen atom abstraction in the crystalline state, but that the resulting biradical **2A** reverts to starting material by reverse hydrogen transfer faster than it cyclizes or cleaves. This is exactly what is thought to happen in the case of cyclodecanone itself, where cyclobutanol formation is observed only in *tert*-butanol,[5] a solvent known to retard reverse γ-hydrogen transfer by hydrogen bonding to the hydroxyl group of the 1,4-hydroxybiradical.[14] Irradiation of cyclodecanone in the non-polar solvent cyclohexane gives no cyclobutanol; instead, an unusual ε-hydrogen abstraction reaction leading to *cis* and *trans* 9-decalol is observed.[4] Such a reaction is of course impossible in the case of 1,6-cyclodecanedione, and in the crystalline state, biradical **2A** experiences no retardation of reverse hydrogen transfer. As a result, no net photochemistry is observed in this medium. The reluctance of biradical **2A** to cyclize is probably related to the well known difficulty involved in forming 8-membered rings[15]

According to the analysis thus far, 1,6-cyclodecanedione should, like cyclodecanone, undergo Yang photocyclization in *tert*-butanol, yet it does not. A clue to the factor responsible for this lack of reactivity comes from the work of Dale et al. on the infrared spectra of 1,6-cyclodecanedione.[16] These authors noticed that the infrared spectrum of this material in the solid state is completely different from that in solution, a result that was attributed to a change in conformation accompanying dissolution. This is an unusual suggestion, because conformationally flexible molecules generally crystallize in or near their lowest energy conformations - the same conformations that are favored thermodynamically in solution. Based on the low dipole moment of 1,6-cyclodecanedione, which suggested that its carbonyl groups are in close intramolecular association, Dale *et al.* proposed the twist-chair-chair-chair or "crown" conformer **1B** (Scheme 1) as the dominant species present in solution. Later variable temperature ^{13}C and ^{1}H NMR studies of 1,6-cyclodecanedione by Anet and co-workers supported this assignment.[17] Transannular C-H...O contacts involving the δ-hydrogens (dotted lines, structure **1B**) were advanced as a possible source of the stabilization of this conformer.[16]

In order to provide additional information on these points, we carried out MM2 calculations on 1,6-cyclodecanedione. These calculations revealed that the crown conformer **1B** is, as hypothesized by Dale,[16] the minimum energy conformation of this molecule. The boat-chair-boat conformation **1A** was found to lie 11.9 kJ/mole above **1B**, and a third conformer, twist-boat-chair-chair form **1C** (Scheme 1), was located between these two at 9.9 kJ/mole. No other conformers were present within a 20 kJ/mole window above the minimum.

These results reveal the probable reason for the failure of 1,6-cyclodecanedione to give any γ-hydrogen abstraction-derived photoproducts in *tert*-butanol - *there are no accessible γ-hydrogens in the lowest energy conformer 1B.* As shown in Scheme 1, the γ-hydrogens in this conformer are either on the wrong side of the ring or are pointing directly away from the oxygen atoms, thus preventing abstraction. Conformer **1C** has one potentially abstractable hydrogen atom (dotted lines, Scheme 1), and like conformer **1A**, should be photoreactive in *tert*-butanol. By equating the MM2-derived conformational energies with ΔG° values, the conformer distribution at 25 °C can be calculated to be approximately 97% conformer **1B**, 2% conformer **1C** and 1% conformer **1A**. If we assume that conformers **1A** and **1C** *do* react in *tert*-butanol with quantum yields of approximately 15% (the same as that for 1,9-cyclohexadecanedione under the same conditions[18]), the effective overall type II quantum yield for 1,6-cyclodecanedione might be around 0.005, close to our detection limit. Compounding the problem is the fact that secondary photolysis of the primary photoproduct is a distinct possibility, since the expected cyclobutanol still contains a potentially photoreactive ketone group. It is therefore not surprising that no discrete photoproducts could be detected or isolated under these conditions.

Raising the temperature should increase the concentrations of the potentially reactive conformers **1A** and **1C**, albeit only slightly. Nevertheless, we thought it worthwhile to try a photolysis in *tert*-butanol at 80 °C. At this temperature, the conformer population is predicted to be approximately 95% **1B**, 3% **1C** and 2% **1A**. By carrying out the photolysis under these conditions in the presence of a photochemically unreactive internal standard (heptadecane), it was possible to detect a very slow loss of parent diketone. GC analysis of the reaction mixture showed the development of a large number of very small peaks, none of which integrated to more than a few tenths of a percent of the total. Control experiments demonstrated that 1,6-cyclodecanedione is stable in hot *tert*-butanol in the dark.

The molecular mechanics results show that, as suggested by Dale,[16] the δ-hydrogen atoms of conformer **1B** are indeed in close transannular contact with the carbonyl oxygen atoms. Our calculations indicate a C-H...O distance **d** of 2.67 Å with $\omega = 63°$, $\Delta = 92°$ and $\theta = 102°$. The question then arises as to why photochemical δ-hydrogen atom abstraction and cyclopentanol formation are not observed in solution, particularly when analogous processes have been well documented elsewhere.[19] There appear to be two main answers to this question. First, the hydrogen atoms in question are α with respect to the non-abstracting carbonyl group and are therefore deactivated towards abstraction by the transannular carbonyl group, which becomes strongly electrophilic upon excitation. Wagner and co-workers have documented similar effects for γ-hydrogen abstraction.[20] Secondly, δ-hydrogen abstraction is generally much slower than the stereoelectronically favored γ-process.[21] Analysis of the δ-hydrogen abstraction reaction in crown conformer **1B** according to the molecular mechanics protocol discussed above reveals that this reaction is clearly unfavorable, with a Δ SE of 6.0-6.3 kcal/mole.

We turn next to the interesting question of why 1,6-cyclodecanedione prefers the crown conformation **1B** in solution rather than the more usual boat-chair-boat form **1A**. As mentioned previously, Dale advanced the hypothesis, with no discussion, that this was due to attractive transannular C-H...O interactions involving the δ-hydrogens.[16] This was a prescient suggestion since at the time, the very existence of C-H...O interactions was the subject of considerable debate, and although today their presence is well accepted,[22] they are almost always invoked to explain crystal packing phenomena, not fluid phase conformational equilibria. They have, however, been suggested to be important in determing the rotamer populations of non-cyclic aliphatic ketones,[23] and on the basis of MP2/6-31G* calculations on the interaction between methane and formaldehyde, Wiberg *et al.* concluded that there is an energy minimum at an O...H distance of 2.58 Å.[24] Wiberg also pointed out that C-H...O interactions become more important as the C-H bond becomes more acidic.[24] This factor increases the likelihood of C-H...O interactions in the case of conformer **1B**, where the hydrogens in question are α to the carbonyl groups.

We would like to propose that a second interaction that is important in stabilizing crown conformer **1B** in solution is the dipole-dipole attraction between the two carbonyl groups (dashed lines, Scheme 1). The molecular mechanics results indicate that the ketone groups of conformer **1B** have a coplanar, head-to-tail orientation with a non-bonded C...O distance of 3.08 Å, somewhat less than the sum of the van der Waals radii for carbon and oxygen (3.22 Å).[25] The corresponding distance for conformer **1A** is 4.19 Å (X-ray value) and those for conformer **1C** are 3.41 and 3.66 Å. As a result, the electrostatic component of the total strain energy from the MM2 calculations is relatively large and negative for conformer **1B** (-6.13 kJ/mole) compared to the values for conformers **1A** (0.22 kJ/mole) and **1C** (-1.98 kJ/mole). This interaction does not show up in the infrared spectrum, however. In carbon tetrachloride, 1,6-cyclodecanedione has the same carbonyl stretching frequency (1713 cm^{-1}) as diametric diketones that lack such arrangements, e.g., 1,8-cyclotetradecanedione and 1,9-cyclohexadecanedione. Similarly, 1,6-cyclodecanedione exhibits essentially identical absorption and fluorescence spectra as its higher homologues, a result that tends to rule out possible intramolecular excimer formation and/or oxygen interchange[26] as a source of its unreactivity in solution. In comparing the phosphorescence spectra of the three diketones, however, that of 1,6-cyclodecanedione is clearly the weakest.

Which factor is more important in stabilizing conformer **1B** in solution - attractive C=O...H interactions as suggested by Dale or the dipole-dipole attraction between the carbonyl groups? We tend to favor the latter for the simple reason that both **1A** and **1C** have the same number of close C=O...H contacts as conformer **1B** (four), yet have signficantly higher conformational energies. Conformer **1A** (the solid state conformer) has two C=O...H_δ contacts at 2.78 Å and two C=O...H_γ contacts at 2.74 Å (X-ray values). Conformer **1C** has three C=O...H_δ contacts at 2.48, 2.67 and 2.79 Å as well as one C=O...H_γ contact at 2.52 Å (MM2 values). Conformer **1B**, on the other hand, is unique among the three in having a sub-van der Waals C=O...C=O interaction, and this would appear to be the deciding factor.

As mentioned above, conformationally flexible molecules generally crystallize in or near their lowest energy conformations, yet 1,6-cyclodecanedione prefers the significantly higher energy boat-chair-boat conformer **1A** in the solid state. Why? One possibility is that conformer **1A** might be favored in the crystal by attractive *inter*molecular C=O...C=O interactions. The carbonyl groups of conformer **1A** (unlike those of conformer **1B**) are free of intramolecular electrostatic contacts, and might therefore be more available to attract other carbonyl groups intermolecularly. The crystal structure of 1,6-cyclodecanedione does not support this picture, however. The packing diagram shows that the carbonyl groups on adjacent molecules are non-interacting.

In their 1972 paper, Dale et al. noted that, compared to other diametric diketones, 1,6-cyclodecanedione had unusually large values of the enthalpy and entropy of melting, thus indicating the presence of particularly strong packing forces.[16] Our X-ray crystallographic results support this conclusion. The calculated crystal density of 1,6-cyclodecanedione is 1.240 g/cm^3, approximately 15-20% higher than the other diametric diketones whose crystal structures we have determined.[1-3] The packing forces that favor the crystallization of 1,6-cyclodecanedione in the higher energy boat-chair-boat form **1A** are probably related to the fact that this conformer is more spherical and fills space better than the more extended conformers **1B** and **1C**. In addition, and perhaps more importantly, the crystal structure indicates that there is an extensive network of close *inter*molecular C=O...H contacts in this case. Each oxygen atom of conformer **1A** has no less than five C=O...H contacts under 3 Å with a neighboring molecule. The three closest of these, at 2.65, 2.77 and 2.86 Å, involve interactions with the relatively acidic α-hydrogens. These contacts probably account for the unusually low carbonyl stretching frequency exhibited by 1,6-cyclodecandione in the solid state (1688 cm^{-1}) compared to those of other diametric diketones (1700-1705 cm^{-1}).

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged. We thank Professor L.S. Weiler for helpful discussions and assistance with the MM2 calculations and Dr.

Gregory W. Sluggett for help in measuring the fluorescence and phosphorescence spectra.

REFERENCES AND FOOTNOTES

---

1. Lewis, T.J.; Rettig, S.J.; Scheffer, J.R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1990**, *112*, 3679.
2. Lewis, T.J.; Rettig, S.J.; Scheffer, J.R.; Trotter, J. *J. Am. Chem. Soc.* **1991**, *113*, 8180.
3. Lewis, T.J.; Rettig, S.J.; Scheffer, J.R.; Trotter, J. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 17.
4. Bernard, M.; Yang, N.C. *Proc. Chem. Soc.* **1958**, 302.
5. Sauers, R.R.; Huang, S-Y. *Tetrahedron Lett.* **1990**, *31*, 5709.
6. Urry, W.H.; Trecker, D.J.; Winey, D.A. *Tetrahedron Lett.* **1962**, 609.
7. Hückel, W.; Danneel, R.; Schwartz, A.; Gercke, A. *Ann.* **1929**, *474*, 121.
8. Germain, G., personal communication as reported by Dunitz, J.D. In *Perspectives in Structural Chemistry*; Dunitz, J.D., Ibers, J.A., Eds.; Wiley: New York, 1968; Volume 2; p. 495. Our own X-ray diffraction study, from which the data reported in the present paper are taken, confirms this assignment.
9. Dunitz, J.D. *Pure Appl. Chem.* **1971**, *25*, 495.
10. Scheffer, J.R. In *Organic Solid State Chemistry*, Desiraju, G.R., Ed.; Elsevier: Amsterdam, 1987; Chapter 1; pp. 1-45.
11. (a) Sauers, R.R.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1989**, *30*, 527; (b) Sauers, R.R.; Stevenson, T. *J. Org. Chem.* **1992**, *57*, 671.
12. Sauers, R.R.; Edberg, L.A. *J. Org. Chem.* **1994**, *60*, 7061.
13. Owing to changes in the parameter set, the numbers quoted here for cyclodecanone differ slightly from those originally published in reference 5.
14. Wagner, P.J.; Kochevar, I.; Kemppainen, A.E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
15. Illuminati, G.; Mandolini, L. *Acc. Chem. Research* **1981**, *14*, 95. Interestingly, 1,4-biradical cyclization *is* observed in the case of cyclodecan-1,2-dione, even in the non-hydrogen bonding solvent benzene.[6] It may be that reverse hydrogen transfer is retarded in this case by intramolecular hydrogen bonding to the adjacent ketone oxygen.
16. Alvik, T.; Borgen, G.; Dale, J. *Acta Chem. Scand.* **1972**, *26*, 1805.
17. Anet, F.A.L.; St. Jacques, M.; Henrichs, P.M.; Cheng, A.K.; Krane, J.; Wong, L. *Tetrahedron* **1974**, *30*, 1629.
18. Scheffer, J.R.; Gudmundsdottir, A.D., unpublished results.
19. Wagner, P.J. *Acc. Chem. Research* **1989**, *22*, 83.
20. Wagner, P.J.; Kemppainen, A.E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.
21. Wagner, P.J. *Acc. Chem. Research* **1972**, *4*, 168.
22. (a) Desiraju, G.R. *Acc. Chem. Research* **1991**, *24*, 290; (b) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

23. Zushi, S.; Kodama, Y.; Nishihata, K.; Umemura, K.; Nishio, M.; Uzawa, J.; Hirota, M. *Bull Chem. soc. Jpn.* **1980**, *53*, 3631.
24. Wiberg, K.B.; Waldron, R.F.; Schulte, G.; Saunders, M. *J. Am. Chem. Soc.* **1991**, *113*, 971.
25. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
26. Yang, N.C.; Eisenhardt, W.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 4030.