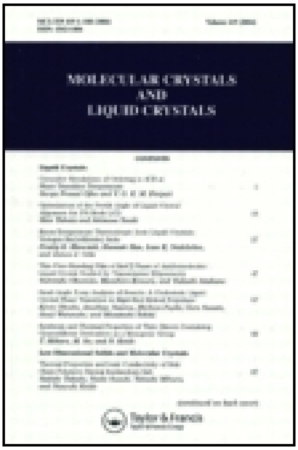


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Topochemical Reactions of Metal Complexes of Substituted Benzylidenecyclopentanones

Charis R. Theocharis [a] , Alison M. Clark [a] , Sian E. Hopkin [a] , Peter Jones [a] , Adrian C. Ferryman [a] & Francis Usanga [a]

[a] Department of Chemistry, Brunei University, Uxbridge, Middlesex, UB8 3PH, UK

To cite this article: Charis R. Theocharis , Alison M. Clark , Sian E. Hopkin , Peter Jones , Adrian C. Ferryman & Francis Usanga (1988): Topochemical Reactions of Metal Complexes of Substituted Benzylidenecyclopentanones, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 156:1, 85-91

To link to this article: http://dx.doi.org/10.1080/00268948808070557

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 156, pp. 85-91
Reprints available directly from the publisher.
Photocopying permitted by license only.

Printed in the United States of America

TOPOCHEMICAL REACTIONS OF METAL COMPLEXES OF SUBSTITUTED BENZYLIDENECYCLOPENTANONES

CHARIS R. THEOCHARIS*, ALISON M. CLARK, SIAN E. HOPKIN,
PETER JONES, ADRIAN C. PERRYMAN, and FRANCIS USANGA
Department of Chemistry, Brunel University, Uxbridge,
Middlesex, UB8 3PH, UK.

Abstract The 2,5-dibenzylidene and 2-benzylidene cyclopentanone frameworks have been modified, the first by incorporation of OH groups on the two phenyl groups, the second by adding a malonic group at the 3-position of the five member ring, so as to act as ligands. Changes in packing, and hence reactivity, can now be achieved by changing the coordinated transition metal cation. The malonic group imparts novel modes of solid state photoreactivity.

INTRODUCTION

Progress has been achieved in the determination of the factors that control the packing of organic molecules in crystals, through the systematic study of closely related structures[1,2]. One such study employed 2-benzyl-5-benzylidene cyclopentanone (BBCP)[3-5] and 2,5-dibenzylidene cyclopentanone (DBCP, 2, see Table I)[6-9] and their various analogues. These compounds exhibit typical [2+2] photocycloaddition behaviour involving the exocyclic double bonds. The usefulness of adducts of DBCP and of 2,5-dibenzylidene acetone with uranyl ions in crystal engineering has been previously demonstrated[10]. In these adducts, the uranium ion is bonded to two organic moieties via their carbonyl groups. However, the photochemistry of coordination compounds and the possibility of using metal ions to control the crystalline packing of enones had not been studied hitherto. The BBCP and DBCP framework can easily be modified (e.g. 3-8) so as to act as ligands. Thus, variations in the packing motif and hence reactivity can be achieved by changing the central metal ion in the complex (9)[11].

It can be seen from the Table that ligands based on DBCP can be divided into two types, those in which the metal is bonded to groups in conjugation with the dimerisable double bonds, and those in which no such conjugation exists. Comparison between the behaviour of the two groups will help determine the influence of the metal ion on the intrinsic photochemistry of the benzylidene moieties. The molecular structure of the first group suggests the possibility of the formation of coordination polymers (e.g. 10) with extended conjugation systems which might be expected, in favourite cases (i.e. for a judicious choice of metal and substituents on the DBCP framework), to be semiconducting. The conjugation would involve the pi system of the benzylidene cyclopentanone moieties and the appropriate half-filled d orbitals on the metal ions. Similar coordination and organometallic polymers have been shown to exhibit semi and metallic conductivity[12].

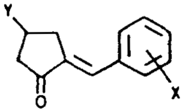
EXPERIMENTAL

3,4- and 2,3-dihydroxydibenzylidene cyclopentanone were prepared as previously described[7,8] from cyclopentanone and the appropriate benzaldehyde, using methanolic KOH as catalyst. It was, however, found to be necessary to protect the hydroxyl groups during reaction by conversion to the butyl ether. The required compound was then obtained by

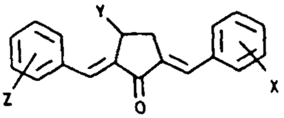
TABLE I

Molecule	Framework	X	Y	Z	M	Type of reactivity
1	1	H	H	-	-	D
2	2	H	H	H	-	D
3	2	3,4OH	H	3,4OH	-	D
4	2	2,3OH	H	2,3OH	-	D
5	1	H	MALONIC	-	-	CD
6	2	H	MALONIC	H	-	H
7	1	H	MALONIC	-	Cu^{2+}	D
8	2	H	MALONIC	H	Cu^{2+}	-
9	2	2,3OH	H	2,3OH	Ni^{2+}	D
10	2	2,3OH	H	2,3OH	Cu^{2+}	D
11	2	2,3OH	H	2,3OH	Zn^{2+}	-
12	2	3,4OH	H	3,4OH	Ni^{2+}	D

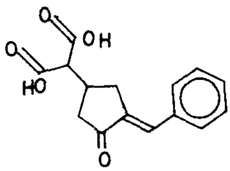
Keys: D -dimerisation, C -decarboxylation, H -dehydration.



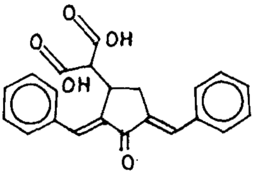
1



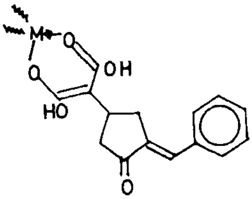
2



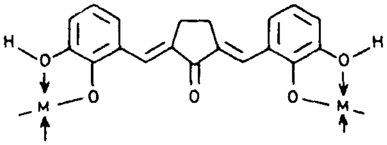
5



6



7



10

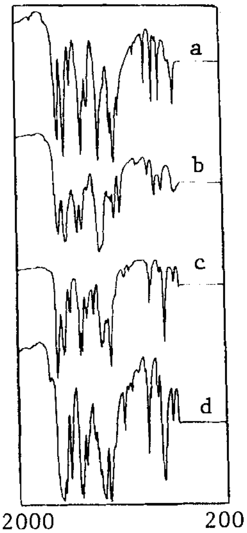


FIGURE 1

FTIR spectra in the 200-2000 cm^{-1} region.
a = compound 2, b = 9,
c = 10, d = 11.

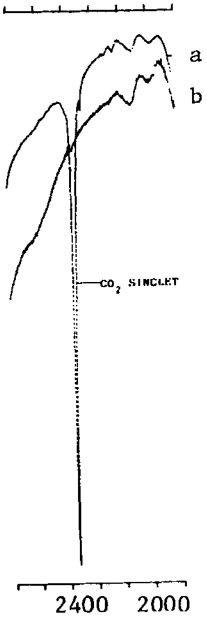


FIGURE 2

FTIR spectra of compound 5.
a - after irradiation
b - before irradiation

removal of the butyl groups by reaction with anhydrous aluminium chloride and then water. 3-Malonic cyclopentanone was prepared from the reaction of diethyl malonate and 2-cyclopentenone in the presence of ethoxide. The product was worked up in dilute acid. Subsequent reaction with benzaldehyde led to the dibenzylidene system. Reaction of cyclopentenone with benzaldehyde followed by reaction with diethyl malonate led to the monobenzylidene series of compounds. Complexation with the appropriate metal ion was carried out in a methanol solution. In some cases it was found necessary to add a drop of ammonia, in order to make the pH of the solution conducive to complexation. Recrystallisation was carried out from chloroform methanol solutions.

FTIR spectra were recorded from kBr discs using a 1710 FTIR spectrometer. Photochemical reactions were carried out using a pyrex filtered 500W low pressure mercury vapour lamp.

DISCUSSIONS

Several of the compounds studied underwent light-induced [2+2] topochemical cycloaddition of the exocyclic double bond, whilst others exhibited novel types of reactivity (see later and Table I), whereas several others were found to be photostable. All coordination compounds prepared thus far, were polycrystalline, and therefore no crystallographic study was possible. Structural and reactivity studies were carried out by FTIR.

Compounds 9-12 appear to be polymeric. Compound 3 and 4 were found to be photodimerisable, as were their Ni^{2+} and Cu^{2+} complexes. Conversely, the Zn^{2+} complex for both compounds were found to be photostable. Comparison of the infrared spectra (see Figure 1) of the complexes of a given compound indicated significant differences. The spectra of compounds 3 and 4 were significantly different from those of their complexes. Given that the metal ions used were of very similar atomic weights, it is logical to assume that any differences in the IR spectra were due to differences in the crystalline packing. This, may, in part, be due to differences in the local geometry round the metal ion. That differences in packing do occur can be seen from the different behaviour vis a vis photoirradiation of the Zn^{2+} complexes as compared with the others. Conductivity studies of the Ni^{2+} complex indicated this to be an insulator.

Compounds 5 and 6 exhibited, in addition to photodimerisation for 5, two unexpected types of solid-state photochemical reactivity, namely that of decarboxylation for 5 and dehydration for 6, both involving the malonate group. In addition, 3-malonic cyclopentanone also exhibits solid state decarboxylation. Carbon dioxide evolved during decarboxylation gave rise to a single narrow peak in the FTIR spectrum, indicating that CO_2 molecules remained trapped within the reacting crystallites. Figure 2 shows the region of CO_2 absorption in the ir spectrum for compound 5 upon irradiation. The close chemical similarities of the malonic groups on compounds 5 and 6 suggests that both these photochemical reactions were under lattice control and that the difference in reactivity reflects differences in packing. It is hoped that crystallographic studies will help elucidate the mechanisms for these reactions. Comparison of the FTIR spectra of 5 before and after irradiation shows no appeciable increase in the width of any of the peaks. This appears to suggest that crystallinity is maintained during decarboxylation.

The financial assistance of the University via the BRIEF system, and useful discussions with Dr M. Muir are appreciated.

REFERENCES

1. G. M. J. Schmidt, Pure Appl. Chem., 27, 637, (1971).
2. J. M. Thomas, Pure. Appl. Chem., 51, 1065, (1979).
3. W. Jones, H. Nakanishi, C. R. Theocharis and J. M. Thomas, J. Chem. Soc. Chem. Comm., 610, (1980).
4. H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse and M. Motevalli, J. Phys. Chem., 85, 3636, (1981).
5. J. M. Thomas, Nature, 289, 633, (1981).
6. S. K. Kearsley, PhD Thesis, University of Cambridge, (1984).
7. C. R. Theocharis, W. Jones, J. M. Thomas, M. Motevalli and M. B. Hursthouse, J. Chem. Soc. Perkin Trans 2, 71, (1984).
8. G. Kaupp and I. Zimmerman, Angew. Chem. Int. End. Eng., 20, 1018, (1981).
9. C. R. Theocharis, J. M. Thomas and W. Jones, Mol. Cryst. Liq. Cryst., 93, 53, (1983).
10. A. Mustafa, Chem. Rev., 51, 1, (1952).
11. C. R. Theocharis, J. Chem. Soc. Chem. Comm., 80, (1987).
12. A. R. Blythe, Electronic Properties of Polymers, Cambridge University Press, (1979).