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

A Molecular Orbital Study of 6:1 1,3-Dione Complexes with Fluorinated Benzenes

Laszlo Turi [a b] & J. J. Dannenberg [a b]

[a] Department of Chemistry, City University of New York - Hunter College

[b] The Graduate School, 695, Park Avenue, New York, NY, 10021

Version of record first published: 24 Sep 2006.

To cite this article: Laszlo Turi & J. J. Dannenberg (1992): A Molecular Orbital Study of 6:1 1,3-Dione Complexes with Fluorinated Benzenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 219:1, 63-69

To link to this article: http://dx.doi.org/10.1080/10587259208032117

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 63–69
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A MOLECULAR ORBITAL STUDY OF 6:1 1,3-DIONE COMPLEXES WITH FLUORINATED BENZENES

LASZLO TURI AND J. J. DANNENBERG*

Department of Chemistry, City University of New York - Hunter College and The Graduate School, 695 Park Avenue, New York, NY 10021

(Received November 7, 1991; in final form December 5, 1991)

Abstract The hydrogen bonding interactions of 6:1 cyclamers composed of 1,3-diones in their enol forms and both fluoro- and perfluorobenzene have been examined by the AM1 molecular orbital method. These structures are analogous to those found experimentally in cocrystals of benzene with these diones. The fluorobenzne host-guest complexes are predicted to be stable, but the perfluorobenzene complexes are not. However, it is unlikely that the stabilization of fluorobenzene in the cocrystal would be greater than the interaction between molecules of fluorobenzene in solution.

Keywords: AM1 calculations, 1,3-Dione complexes, Molecular orbital study, Hydrogen bond, Benzene, Host-guest complex

INTRODUCTION

We have recently conducted a molecular orbital (AM1 and ab initio) study of the aggregation of 1,3-cyclohexanedione (CHD) and a frozen structure of 1,3-propanedione (PPD).[1] This study included a novel crown ether-like host-guest species, the 6:1 1,3-cyclohexanedione:benzene cyclamer,whose crystal structure has been determined by Etter.[2]

In this paper we report a molecular orbital study of the interactions between fluorobenzene and perfluorobenzene with the same host (CHD and PPD) as in our previous study.

METHODS

We have used the semiempirical AM1 molecular orbital method[3] for these studies. Several successful hydrogen-bonding studies using the AM1 method have been reported.[4] Accurate ab initio calculations are not computationally practical on systems as large as those under study here. In addition, small basis set Hartree-Fock (HF) calculations are not generally reliable for H-bonding interactions. Previously conducted ab initio calculations with the small basis set, 6-31G,[1] on the 6:1 PPD:benzene cyclamer are used for comparison with the AM1 results.

The calculations have been done with the following restrictions: In all complexes the hydrogen-bonded skeleton composed of sp^2 carbon atoms, carbonyl oxygen atoms and hydroxy groups was kept planar. The aromatic rings in the centers of the cyclamers were also held in this plane. An axis of symmetry was imposed upon the geometry of each of the aggregates, except for those containing fluorobenzene as the aromatic, where the symmetry was relaxed for the fluorobenzene only. This axis is six-fold for the PPD and three-fold for the CHD cyclamers (where the pucker of the rings points in opposite directions in adjacent enols), respectively.

RESULTS AND DISCUSSION

Figure 1 shows the structure of PPD:benzene cyclamer, previously reported. Each aromatic hydrogen is directed toward a carbonyl oxygen atom of an enol. The hydrogen-bonding patterns of the CHD:benzene and DMC:benzene complex are very similar, as expected. The only significant geometric differences arise from the ring pucker of the cyclic enols. In principle, the cyclamer can assemble with the C_5 of adjacent enols pointing in the opposite directions (as observed experimentally) or in a variety of other patterns including

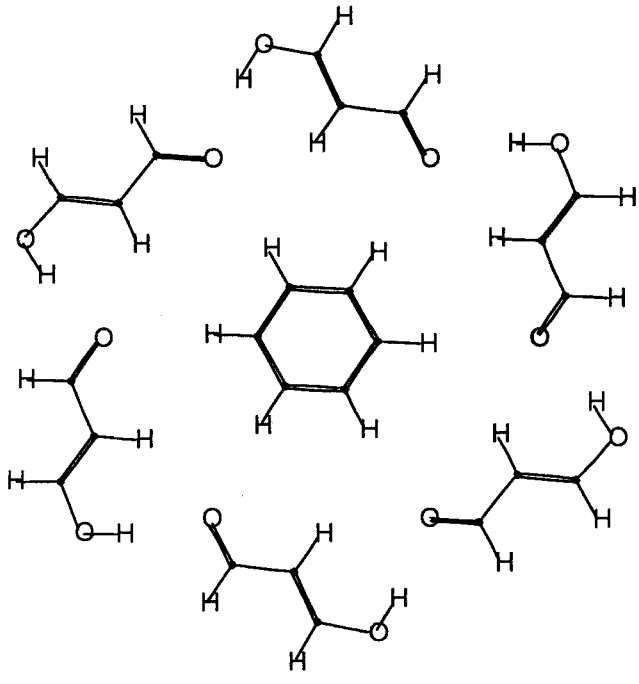
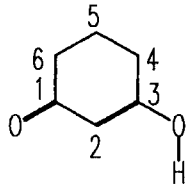


Figure 1

all C_5's pointing in the same direction. AM1 calculations on the two extreme cases for CHD indicated no energetic preference for either pattern. Therefore all further calculations maintained the experimentally determined pattern. Table 1 displays the calculated energies for the various species. AM1 predicts interaction energies for the association of benzene with a cyclic hexamer of the enols of about -3.1 kcal/mol. This interaction increases slightly in the order PPD < CHD < DMCHD. The ab initio (6-31G) value of -4.1 kcal/mole for the interaction energy of benzene with PPD reported earlier is in good agreement with the AM1 results. This magnitude of the stabilization would be lowered slightly if completely corrected for zero point vibrational error and basis set superposition error. The 6-31G total hydrogen bonding interaction energy for the six enols in the cyclamer (without benzene), -90.4 kcal/mol, is significantly greater than the AM1 value of -30.5 kcal/mol. Presumably in this case the AM1 method underestimates the strength of these hydrogen-bonds.

The calculated and experimental geometrical parameters are presented in Table 2. The experimental O-O distance in the CHD/benzene complex, 2.579 Å, is unusually short.



		hexamer	hexamer - benzene complex	hexamer - monofluoro benzene complex	hexamer - perfluorobenzene complex
1,3-propane dione	Heat of formation	-436.4	-417.4	-462.1	-668.1
	H-bonding energy	-27.5	-30.5	-29.9	-28.1
1,3-cyclohexane dione	Heat of formation	-521.8	-503.0	-547.3	-752.4
	H-bonding energy	-28.9	-32.0	-31.4	-28.3
5,5-dimethyl-1,3-cyclohexane dione	Heat of formation	-563.5	-544.6	-589.1	-794.0
	H-bonding energy	-29.1	-32.3	-31.4	-28.4

Table 1 Total and interaction energies (kcal/mol)

The calculated AM1 O-O distance in the PPD/benzene complex is 3.015 Å, which is significantly longer. The 6-31G calculations predicted this distance to be 2.642 Å, closer to the experimental value. It is often assumed that the strength of an H-bond can be related to the O-O distance.[5] The longer O-O distances obtained with AM1 are consistent with the lower calculated H-bonding energies.

Table 1 contains the calculated hydrogen-bonding energy values for the complexes of C_6F_6 and C_6H_5F with the diones. These values suggest that C_6F_6 should have a favorable interaction energy with the cyclic six-membered aggregate of PPD, but not CHD or DMCHD. The stabilization with the PPD cyclamer is 0.6 kcal/mole, while the destabilization is 0.6 and 0.7 kcal/mole for CHD and DMC, respectively. Although the results suggest cocrystallization of CHD with C_6F_6 to be unlikely, the hydrogen-bonding pattern of is quite interesting (see figure 2). Comparison of this structure with the analogous benzene complex indicates the C_6F_6 to be rotated by about 22° relative to the benzene in its complex. Each

STRUCTURE		Geometric parameters (Å)					
		C_1-C_2	C_2-C_3	C_1=O	C_3-O	O-O	cavity[a]
1,3-propanedione	hexamer	1.451	1.350	1.239	1.355	3.019	10.890
	heamer - benzene	1.450	1.350	1.239	1.356	3.015	10.155
	hexamer (6-31G)	1.428	1.345	1.235	1.323	2.639	11.331
	hexamer - benzene (6-31G)	1.427	1.345	1.236	1.323	2.642	11.237
	hexamer - monofluorobenzene	1.451	1.350	1.239	1.356	3.013	10.359
	hexamer - perfluorobenzene	1.452	1.351	1.239	1.355	3.021	11.612
1,3-cyclohexane dione	hexamer	1.455	1.354	1.243	1.363	3.009	10.591
	hexamer - benzene	1.454	1.354	1.244	1.363	3.009	10.327
	hexamer - monofluorobenzene	1.455	1.354	1.243	1.364	3.007	10.388
	hexamer - perfluorobenzene	1.456	1.354	1.242	1.363	3.016	11.139
1,3-cyclohexane dione	hexamer - benzene experimental	1.413	1.349	1.253	1.318	2.579	-
5,5-dimethyl-1,3-cyclohexanedione	hexamer	1.454	1.354	1.244	1.364	3.009	10.588
	hexamer - benzene	1.454	1.354	1.244	1.364	3.008	10.344
	hexamer - monofluorobenzene	1.455	1.354	1.243	1.364	3.007	11.128
	hexamer- perfluorobenzene	1.454	1.354	1.244	1.364	3.017	10.387
[a]Distances between carbonyl oxygens on enols opposite to each other.							

Table 2 Selected geometric parameters of the complexes.

fluorine atom is directed toward an H attached to C_2 on one of the enol monomers. These hydrogens are appreciably positive (0.172 by AM1). Despite these favorable interactions, C_6F_6 does not interact favorably with the CHD and DMC complexes. This may be due to the longer C-F bond relative to C-H in benzene, which would tend to push the enols away from each other. The cavities of the clyclamers contract upon insertion of C_6H_6 or C_6H_5F, but expand upon the insertion of C_6F_6. The O-O distances in the perfluorobenzene and benzene aggregates remain similar (Table 2).

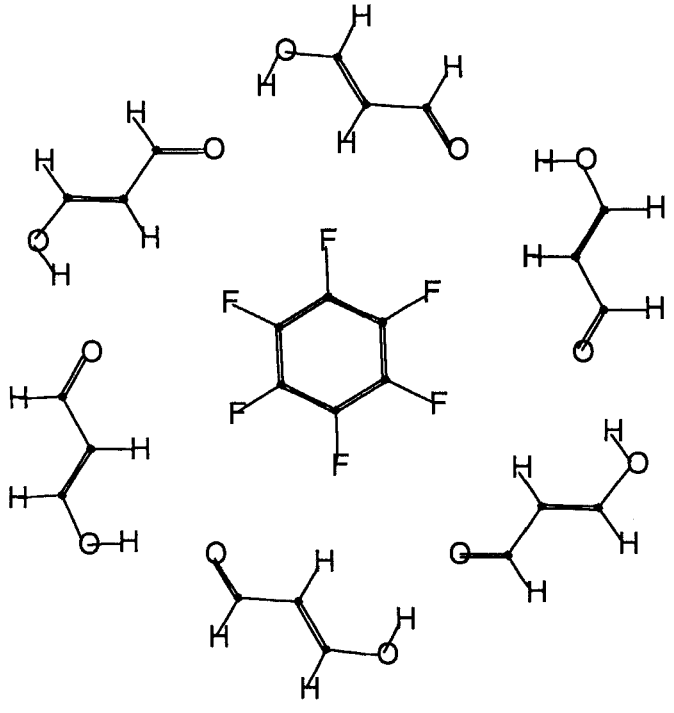


Figure 2

The cocrystal of C_6H_5F with PPD is predicted to be stablized by 2.4 kcal/mol relative to the hexamers. The analogous complexes with CHD and DMCHD are stablized by 2.5 and 2.3 kcal/mol, respectively. However these cocrystals must compete with aggregation of C_6H_5F (which has a significant dipole moment) in solution. The fluorine atom in these structures must have an unfavorable interaction with an oxygen in order for the five aromatic hydrogens to remain in position to H-bond with the adjacent enols. This might create a kinetic problem since the enol facing the fluorine would likely be the last to attach.

CONCLUSION

Molecular orbital calculations on 6:1 of CHD or and DMCHD with fluorobenzene or perfluorobenzene suggest that, unlike the case of benzene, cocrystallization of CHD or DMCHD with these molecules is unlikely.

ACKNOWLEDGEMENT

Partial support for this work was provided by the PSC-BHE, National Science Foundation and the IBM Corporation. We thank Professor Margaret Etter providing the experimental data and for many useful discussions.

REFERENCES

1) L. Turi and J. J. Dannenberg, J. Am. Chem. Soc., submitted for publication.

2) M. C. Etter, Z. Urbanczyk-Lipkowska, D. A. Jahn, and J. S Frye, J. Am. Chem. Soc., 108, 5871 (1986).

3) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, J. Am. Chem. Soc., 107, 3902 (1985).

4) a) J. J. Dannenberg, and L. K. Vinson, J. Phys. Chem., 92, 5635 (1988) ; c) S.Galera, J. M. Lluch, A. Oliva, and J. Bertrán, THEOCHEM, 40, 101(1988); d) L. K.Vinson, and J. J. Dannenberg, J. Am. Chem. Soc., 111, 2777 (1989).

5) J. Emsley, Chem. Soc. Rev., 9, 91 (1980).