Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Isotope Effect on the Phase Transition Temperatures in Aromatic Hydrocarbon-Tetracyanobenzene Complexes

N. S. Dalal [a], J. A. Ripmeester [a], A. H. Reddoch [a] & D. F. Williams [a]
[a] Division of Chemistry, National Research Council of Canada, Ottawa, Canada

Version of record first published: 08 Feb 2011.

To cite this article: N. S. Dalal, J. A. Ripmeester, A. H. Reddoch & D. F. Williams (1978): Isotope Effect on the Phase Transition Temperatures in Aromatic Hydrocarbon-Tetracyanobenzene Complexes, Molecular Crystals and Liquid Crystals, 49:2, 55-59

To link to this article: http://dx.doi.org/10.1080/00268947808070327

Mol. Cryst. Liq. Cryst. Vol. 49 (Letters), pp. 55-59

Printed in the United States of America

ISOTOPE EFFECT ON THE PHASE TRANSITION TEMPERATURES IN AROMATIC HYDROCARBON-TETRACYANOBENZENE COMPLEXES$^+$

N.S. DALAL, J.A. RIPMEESTER, A.H. REDDOCH, AND
D.F. WILLIAMS
Division of Chemistry, National Research Council of
Canada, Ottawa, Canada

(Submitted for publication July 10, 1978)

It is well established that electrical and magnetic properties of crystals are strongly influenced by structural phase transitions. The strong charge transfer complexes such as tetrathiofulvalene-tetracyanoquinodimethan (TTF-TCNQ) have been intensely studied(1) but much less is known concerning weak charge transfer complexes and the influence of solid-solid transitions on their properties. Typical examples of some weak charge transfer complexes are the 1:1 complexes formed between aromatic donors (e.g. naphthalene) and aromatic acceptors (e.g. 1,2,4,5 tetracyanobenzene, TCNB).

Recent EPR,(2) NMR(3) and Raman(4) studies of these complexes have shown that they undergo structural phase transitions. Typically the crystal structures(5) consist of molecular stacks of alternating donor and acceptor molecules packed face to face. In particular, for naphthalene-TCNB, the room temperature structure is disordered, there being two orientations for each naphthalene, rotated ±18° about the stack axis.(6) There is ^{1}H NMR evidence(3) that the disorder is dynamic and Raman scattering evidence(4) for an order-disorder phase transition at 63K. With a view to finding the major forces which determine the structural change, and hence perhaps better understanding the promoting mechanisms, we are currently studying the influences of isotopic substitution of the donor upon the phase transition temperature T_c. These studies are of interest in view of the current controversy concerning the nature of the phase transitions in biphenyl(7,8), and the weak isotope effect on the Peierls transition temperature of TTF-TCNQ(9). In this letter we wish to report results which show for the first time the large reduction in T_c upon deuteration for several TCNB complexes.

We have studied the 1:1 complexes of naphthalene, naphthalene(d_8), anthracene, anthracene(d_{10}), pyrene and pyrene(d_{10}) with TCNB. Phase transitions of the undeuterated complexes have been reported.(2-4,10,11) We have used NMR, EPR of triplet excitons, Raman scattering and differential scanning calorimetric (DSC) techniques to study this order-disorder transition. All measurements have been made on solution-grown single crystals, and only highly purified components were used. The crystal morphology in all cases agreed with the respective crystal structural data. Unit cell dimensions were also verified by X-ray diffraction, and no evidence of crystal twinning was found, contrary to the report on naphthalene-TCNB.(6) The deuterated hydrocarbons had a certified minimum deuterium content of 98% and their identity was verified with high resolution NMR.

A typical result for anthracene-TCNB and anthracene(d$_{10}$) TCNB from DSC is shown in Fig. 1.

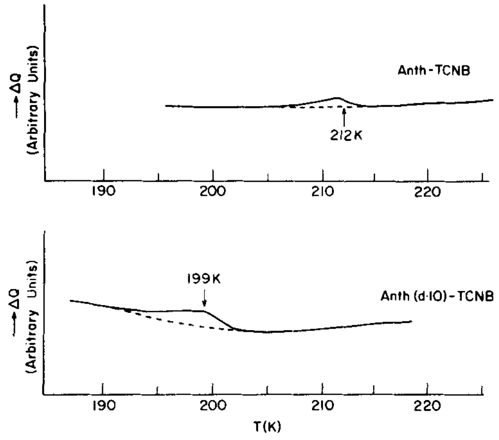

FIGURE 1. Differential scanning calorimetric traces for (a) Anthracene-TCNB and (b) Anthracene (d$_{10}$)- TCNB. The arrows indicate transition temperatures determined from the EPR of triplet excitons.

These thermograms were obtained on a Perkin-Elmer Model DSC-1B calorimeter with heating and cooling rates of 5 and 10°/minute. The thermal hysteresis observed was less than 1°. The peaks in the thermograms were weak but each had a well-defined maximum at a temperature coinciding, to within ±1°, with the phase transition temperature determined from EPR of triplet excitons. For naphthalene-TCNB, the transition temperature, T_c, was deduced from linewidth and intensity changes of intramolecular modes in Raman spectra and from ^1H NMR relaxation times and second moment measurements. For pyrene-TCNB, unusually large (∿40°) thermal hysteresis was observed. This observation explains the large (∿50°) difference between the T_c values reported in earlier studies.(10,11) If single crystals of pyrene (H_{10})-TCNB were used, reproducible peaks in the thermograms at 183±3K, with peak widths ∿1°, were observed on cooling. The crystals always shattered on cooling through this transition temperature. This shattering was also observed visually. On reheating, the thermograms showed several peaks over a range of several degrees around 226K, presumably reflecting the transitions from individual crystallites. For the deuterated samples, the corresponding temperatures were consistently lower, 217 and 175K. It is notable that for polycrystalline samples the peak width was 10-20K, resulting in a far greater scatter in the apparent transition temperatures, in agreement with that reported earlier.(11) The T_c values determined in the present work and those by others are presented in Table 1.

TABLE 1 Phase transition temperatures for the CT complexes of TCNB with various donors.

Donor	Transition Temperature(K)			Methods	Source
	normal	deuterated	diff		
Naphthalene	63±5			Raman	(4)
	69±2	63±2	6	Raman	This work
	72±1			NMR	This work
Anthracene	202			EPR	(2)
	206			EPR, Raman	(2)
	212±2	199±2	13	EPR, DSC	This work
Pyrene	232±1			Calorimetry	(11)
	226±4	217±4	9	DSC(heating)	This work
	183±3	175±3	8	DSC(cooling), visual observation of shattering.	This work

Several interesting conclusions follow from the results of Table 1: (1) Deuteration of the donor causes a significant decrease in T_c. This is relatively unusual, for in many other cases of solid-solid structural transitions, deuteration causes an increase in the transition temperature.(12) (2) For naphthalene-TCNB, the observed T_c value differs from that recently reported.(4) The latter value is actually in agreement with that given here for the deuterated material. Subsequent Raman studies of the transition temperature and vibrational frequencies(13) also indicate that the literature value is based on a deuterated sample. The DSC results for anthracene-TCNB relate to the earlier EPR studies of triplet excitons(2) and to some preliminary Raman work.(2(b)) Relatively sharp peaks in the thermograms show that the sharp changes noted in the EPR spectra and in the intensities of a Raman band(2(b)) at about 202-206K, are indeed related to a change in the long range order rather to a change in the exciton dynamics or some individual molecular motion unrelated to a co-operative phenomenon.

In summary, it has been observed that deuteration of the aromatic donor in complexes with TCNB consistently lowers the solid-solid phase transition temperature. This is in contrast to the increase in T_c generally observed upon H→D isotopic substitution.

References

1. See, for example, A.J. Berlinsky, Contemp. Phys. 17, 331 (1976).
2. (a) A.M.P. Goncalves, Chem. Phys. 19, 397 (1977) and (b) H. Mohwald, E. Erdle and A. Thaer, Chem. Phys. 27, 79 (1978).
3. C.A. Fyfe, D. Harold-Smith and J.A. Ripmeester, J. Chem. Soc. Farad. Trans. II, 72, 2269 (1976); C.A. Fyfe, ibid 70, 1642 (1974).
4. R. MacFarlane and S. Ushioda, J. Chem. Phys. 67, 3214 (1977).
5. F.H. Herbstein, Perspect. Struct. Chem. 4, 166 (1971).
6. S. Kumakura, F. Iwasaki and Y. Saito, Bull. Chem. Soc. Japan 40, 1826 (1967).
7. P.S. Friedman, R. Kopelman and P.N. Prasad, Chem. Phys. Lett., 24, 15 (1974).
8. A. Bree and M. Edelson, Chem. Phys. Letts., 46, 500 (1977).

9. J.R. Cooper, J. Lukatela, M. Miljak, M. Fabre, L. Giral and F. Aharon-Shalom, Solid State Communications 25, 949 (1978).

10. K. Prout, T. Morley, I.J. Tickle and J.D. Wright, J. Chem. Soc. Perkin II, 523 (1973).

11. P.R. Clayton, R.D. Worswick and L.A.K. Staveley, Mol. Cryst. Liq. Cryst. 36, 153 (1976).

12. For examples, see F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon Press, London (1962).

13. H.J. Bernstein, N.S. Dalal, W.H. Murphy, A.H. Reddoch, S. Sunder and D.F. Williams, to be published Chem. Phys. Letts.