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

Transition and Fusion Thermodynamics of Heteroadamantanes

J. T.S. Andrews [a] , R. E. Carpenter [a] , T. M. Martinko [b] [a] , R. C. Fort Jr [c] [a] , T. A. Flood [c] [a] & M. G. Adlington [c] [a]

[a] Liquid Crystal Institute, kent State University, Kent, Ohio, 44242, USA

[b] Department of Chemistry, Hiram College, Hiram, Ohio, 44234, USA

[c] Department of Chemistry, Kent State University, Kent, Ohio, 44242, USA

Version of record first published: 20 Apr 2011.

To cite this article: J. T.S. Andrews , R. E. Carpenter , T. M. Martinko , R. C. Fort Jr , T. A. Flood & M. G. Adlington (1978): Transition and Fusion Thermodynamics of Heteroadamantanes, Molecular Crystals and Liquid Crystals, 41:10, 257-261

To link to this article: http://dx.doi.org/10.1080/00268947808070312

Mol. Cryst. Liq. Cryst. Vol. 41 (Letters), pp. 257-261
© 1978, Gordon and Breach Science Publishers Ltd.
Printed in the United States of America

TRANSITION AND FUSION THERMODYNAMICS OF HETEROADAMANTANES

J.T.S. ANDREWS (*) and R.E. CARPENTER
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 USA

T.M. MARTINKO
Department of Chemistry, Hiram College, Hiram, Ohio 44234 USA

R.C. FORT, Jr, T.A. FLOOD and M.G. ADLINGTON
Department of Chemistry, Kent State University, Kent, Ohio 44242 USA

(Submitted for publication June 8. 1978)

ABSTRACT: We report DSC measurements showing that 2-Oxaadamantane, 2-Thiaadamantane, 2,6-Dioxaadamantane and 2-Oxa-6-Thiaadamantane have orientationally disordered "plastic" phases.

INTRODUCTION

Orientationally disordered ("plastic") crystal phases are exhibited by highly symmetric compact molecules and the entropies of the transitions associated with these phases have been correlated with changes in molecular order. [1] Adamantane has long been known to be a plastic crystal, [2] so we wished to ascertain if molecules structurally similar to adamantane, but with symmetry reduced by the incorporation of one or more hetero-atoms (O- or S- in this case) would show orientationally disordered phases, and if the transition entropies were correlated with the alteration in symmetry.

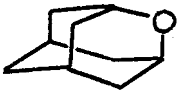
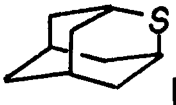
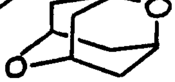
= = = = = = = = = = = =

(*) To whom correspondance concerning this work should be addressed.

MATERIALS

The materials used in this work were prepared using syntheses based upon standard methods, but offering substantially improved overall yields. [3] They were all purified by repeated sublimation until the (sealed tube) melting point became constant. Table 1 lists the materials and illustrates their structures.

TABLE 1 Molecular Structures

Adamantane (ADA)	
2-Oxaadamantane (2OXA)	
2-Thiaadamantane (2THIA)	
2,6-Dioxaadamantane (2,6DIOXA)	
2-Oxa-6-Thiaadamantane (2OXA6THIA)	

CALORIMETRY

Transition temperatures and enthalpies were measured using a Perkin-Elmer differential scanning calorimeter (model DSC-1B) interfaced to, and controlled by, a minicomputer (Digital Equipment Corporation, model PDP-11V03). Sample mass was determined using a Cahn RG electrobalance and all samples were sealed into aluminium calorimetric cells. Fusion of ADA and 2OXA required us to use pressure cells. The analysis of the data was performed by the computer, using programs derived from the Perkin-Elmer "DSC-4" program. [4]

The apparatus was calibrated using indium standards and was then checked by measurement of the transition thermodynamics of diamantane and comparison of the results with those that we had obtained previously by adiabatic calorimetry. [5]

Three of the four transitions in diamantane agreed well both as to temperature and also enthalpy. The temperature of the fourth transition was also in good agreement with the adiabatic result, but the DSC enthalpy was about 10% lower than the adiabatic result, probably for kinetic reasons.

We believe that the temperatures reported here have probable uncertainties of less than 2 K, and that the probable uncertainty of the enthalpy measurements is less than 5%.

RESULTS

Table 2 presents the results of this investigation, listing the transition temperatures and enthalpies and entropies, together with an estimate of the sample purities obtained by analysis of the melting transitions.

TABLE 2 Transition Thermodynamics

	T	H	S	Purity,%
ADA fusion	552	1920	3.47	99.9
trans.	210	707	3.35	
t. Ref.[2]	208.62	807	3.87	
2OXA fus.	567	1940	3.4	99.6
2THIA fus.	597	1937	3.24	99.9
trans.	188-214	465	2.31	
2,6DIOXA fus.	440	903	2.05	99.7
tran.	276	1396	5.05	
2OXA6THIA f.	557	1941	3.48	99.9
t.	224	983	4.40	

Units: Cal., Mol., K

The fusion entropy of each material in the table is less than 5 cal/(mol K), so that each qualifies as a plastic crystal under Timmermann's original criterion. [6] With the exception of 2OXA each also shows a solid state transition which, for ADA at least, has been shown to be associated with the attainment of the plastic state. [7] Since 2OXA and 2THIA show such similar melting behaviour we anticipate that 2OXA will itself undergo transition, but at some temperature below the limit of our instrument (180 K).

The thermodynamic properties of ADA have previously been investigated by adiabatic calorimetry, [2] and we have included these results in Table 2. Whilst the transition temperatures are in good agreement, the DSC enthalpy is more than 10% less than the adiabatic enthalpy. We suspect that kinetic factors are responsible for this, as seemed plausible for the difference between DSC and adiabatic results on one of the four transitions in the related molecule diamantane. [5] Where no kinetic factors intervene, we have found generally good agreement between the two calorimetric techniques.

The values reported in Table 2 for 2OXA are those found for the initial melting of the sample. Subsequent meltings invariably showed a drop in the fusion temperature to 510 K, and a diminution of the fusion enthalpy to 1400 cal./mol. We attempted to clarify the situation by determining the fusion thermodynamics of a freshly triple-sublimed sample of 2OXA. For this sample we observed values consistent with those reported in the table but, on one occasion only, the sample melted initially at 510 K. It seems likely that we are observing the melting of two different crystal forms.

The transitions in 2THIA appeared as a complex of two small endotherms and a large one between 188 and 214 K. The enthalpy and entropy entries for this transition in Table 2 are for the three events taken together.

DISCUSSION

The symmetry reduction brought about by the exchange of methylene groups in ADA by O- or S-atoms does alter the transition entropies. It is puzzling that 2THIA and 2OXA6THIA (which have the same symmetry) show such different transition entropies, and it seems likely that the change in the intermolecular potential has denied some groups of orientations. A true understanding of the transitions will probably need more complete structural information, and a more precise determination of the transitional entropies by adiabatic calorimetry, which we hope to perform in the near future.

ACKNOWLEDGEMENTS

We are happy to acknowledge the generous support of the National Science Foundation (under grant no. ENG76-00046) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. T.M.M. thanks the Trustees of the Paul H. Fall Memorial Fund, of Hiram College, for the award of a Summer Research Studentship. R.C.F. acknowledges a Summer Research Fellowship provided by the Research Council of Kent State University.

REFERENCES

[1] G.B. Guthrie and J.P. McCullough, *J. Phys. Chem.* Solids, 18, 53 (1961).

[2] S.S. Chang and E.F. Westrum, Jr., *J. Phys. Chem.*, 64, 1547 (1960).

[3] R.E. Morland, Ph.D. Dissertation, Kent State University, 1976; R.C. Fort, Jr., R.E. Morland, T.H. Flood and M.G. Adlington, *J. Chem. Soc. Perkin* I, submitted.

[4] Perkin-Elmer Corporation, Norwalk, Conn. U.S.A.

[5] G.M. Spinella, J.T.S. Andrews, R.C. Fort, Jr., W.E. Bacon and J. Sabo, *J. Chem. Thermodynamics*, in press.

[6] J. Timmermanns, *J. Phys. Chem.* Solids, 18, 1 (1961).

[7] R.E. Lechner and A. Heidemann, *Comm. on Physics*, 1, 213 (1976).