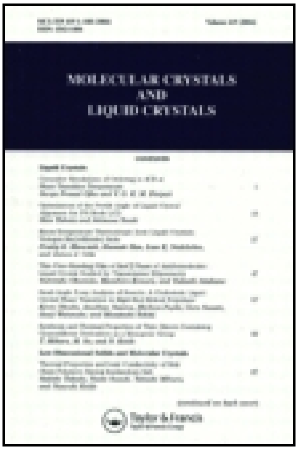

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Loss of Solvent from a Molecular Crystal Solvate. Phenylazotribenzoylmethane Hemietherate

J. D. McCullough Jr. [a] , D. Y. Curtin [a] , L. L. Miller [a] , I. C. Paul [a] & D. B. Pendergrass Jr. [a]
[a] Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois, 61801

Version of record first published: 28 Mar 2007.

To cite this article: J. D. McCullough Jr. , D. Y. Curtin , L. L. Miller , I. C. Paul & D. B. Pendergrass Jr. (1970): Loss of Solvent from a Molecular Crystal Solvate. Phenylazotribenzoylmethane Hemietherate, Molecular Crystals and Liquid Crystals, 11:4, 407-412

To link to this article: http://dx.doi.org/10.1080/15421407008083531

*Molecular Crystals and Liquid Crystals.* 1970. Vol. 11, pp. 407–412

# Loss of Solvent from a Molecular Crystal Solvate. Phenylazotribenzoylmethane Hemietherate†

J. D. McCULLOUGH, JR.,‡ D. Y. CURTIN, L. L. MILLER,
I. C. PAUL§ and D. B. PENDERGRASS, JR.

Department of Chemistry and Chemical Engineering
University of Illinois
Urbana, Illinois 61801

*Received May* 4, 1970; *in revised form July* 1, 1970

## 1. Introduction

In a study⁽¹⁾ of the rearrangement in the solid state of phenylazotribenzoylmethane (I) it was discovered that this compound crys-

$$(C_6H_5CO)_3CN{=}NC_6H_5$$

I

tallizes from diethyl ether as an etherate (II) with the approximate composition $(C_6H_5CO)_3CN{=}NC_6H_5\cdot\frac{1}{2}[(C_2H_5)_2O]$; the ether was lost when the crystals stood for long periods at room temperature. Although many molecules of intermediate size crystallize with the incorporation of solvent molecules,⁽²⁾ little is known about the loss of solvent from such solvates or the structure remaining after the solvent loss. Since the " de-etherated etherate " remaining after the loss of ether from II might show unusual chemical behavior an investigation of the structure of the etherate and the mechanism of loss of ether from single crystals has been undertaken.

---

† We are indebted to the National Science Foundation and the Advanced Research Projects Agency for Partial Support of this work. Taken in part from the Ph.D. Theses submitted to the University of Illinois, by L. L. M. (1964), J. D. M., Jr. (1970) and D. B. P., Jr. (1970).

‡ N. I. H. Biophysical Trainee, 1968–1970.

§ Alfred P. Sloan Research Fellow.

## 2. Experimental

### *Characterization of the Etherate (II) of Phenylazotribenzoylmethane*

The azo compound I was purified by crystallization by the addition of hexane to a solution in ether below room temperature. Recrystallization was repeated until the ultraviolet maximum at 424 nm showed a constant $\epsilon(325 \pm 15)$. Flat yellow platelets o etherate II 1–2 mm in length and with well-developed (010) faces were prepared by cooling a concentrated solution of I in anhydrous ether to 10°. The nmr spectrum in methylene chloride showed the ethyl absorption of the ether as a quadruplet at $\tau$ 6.59 and a triplet at $\tau$ 8.88. Comparison of the total area in this region and the area of the aromatic multiplet at $\tau$ 2.0–2.9 gave a value of the molar ratio of diethyl ether: azo compound I of 0.46–0.56:1. Although carbon analyses showed some variation, a specimen which had stood for 24 hr gave a satisfactory carbon, hydrogen and nitrogen analysis. [Calcd. for $C_{28}H_{20}N_2O_3 \cdot \frac{1}{2}C_4H_{10}O$: C, 76.7; H, 5.3; N, 6.0. Found: C, 77.0; H, 5.3; N, 6.3.]

Two kinds of crystals were common, one " diamond-shaped " and one " blunt-nosed ". While the interfacial angles of the two types were the same, two pairs of faces were developed in the " blunt-nosed " crystals which were absent in the " diamond-shaped " (Fig. 1).

### *Space Group and Unit Cell Parameters*

The space group of II was uniquely determined as $P2_1/c$. Unit cell parameters are presented in Table 1 together with the previously reported⁽³⁾ values for the ether-free azo compound I, prepared by recrystallization from xylene-hexane.

TABLE 1 Unit Cell Parameters for Phenylazotribenzoylmethane⁽³⁾ (I) and its Etherate (II) (Each Space Group $P2_1/c$)

| Crystal | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | $Z$ | $V$ (Å$^3$) |
|---|---|---|---|---|---|---|
| I⁽³⁾ | 13.04(4) | 10.34(4) | 16.51(5) | 90.75(17) | 4 | 2226(22) |
| II | 10.07(2) | 20.63(4) | 13.54(6) | 115.70(17) | 4 | 2534(21) |

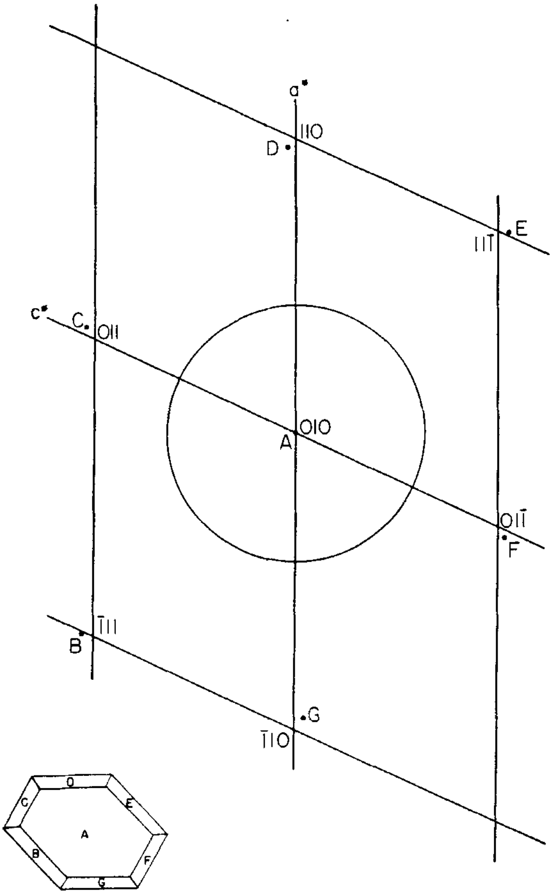

Figure 1. Gnomonic projection of crystals of the etherate of phenylazotribenzoylmethane. Next to the projection is a sketch of a " blunt-nosed " crystal. The " diamond-shaped " crystals differed only in having faces C and F undeveloped.

*Loss of Ether from Phenylazotribenzoylmethane Etherate (II)*

The loss of ether from single crystals of the etherate (II) at room temperature was followed by observation at regular intervals on a microscope stage between crossed polarizing filters. Figure 2 shows a series of photographs of such a crystal taken over a period of more than one month (the illumination is by light transmitted through the crystal). After six days an opaque region appeared at one edge and thereafter spread slowly throughout the crystal; the rate of boundary migration was about 0.014 mm/day. Other crystals became opaque more rapidly; some crops showed a tendency to develop opaque regions simultaneously from several points around the periphery of the crystal. All crystals retained their external shapes on loss of ether. Some still transmitted light when examined with a microscope but showed no extinction when rotated between crossed polarizing filters (see Fig. 2). In certain sufficiently thick crystals the opaque region which began to spread in a layer near the bottom of the crystal moved approximately uniformly in directions normal to the [010] direction but not nearly as rapidly in the [010] direction.

A powder photograph of the etherate freshly ground to a fine powder in the presence of a few drops of ether and placed in a capillary was found to differ markedly from the powder photograph of the azo compound I. After 16 days the etherate crystals had lost a substantial fraction of the incorporated solvent and with the exception of a few lines the powder pattern resembled that of I; after 53 days the powder pattern of the etherate had changed to that of I. A crystal of the etherate II which had been allowed to lose its ether was mounted on the powder camera without being ground and a powder pattern identical to that of the ground crystals was obtained. Powder photographs of " blunt-nosed " and " diamond-shaped " crystals which had lost their ether were identical.

A single crystal of etherate II in a sealed capillary was oriented on a precession camera and the seal broken after photography of the $0kl$ net. The intensities of the reflections diminished gradually (31 photographs over 58 hr) with no new spots developing. A long exposure taken 16 days later showed only diffuse cloudiness together with weak indications of powder rings. Accompanying the loss of intensity of the reflections was a definite change in the shape of the spots which could be correlated with the amount and general shape of intact etherate in the crystal.

## 3. Discussion

While the present results do not describe in detail the structure of the etherate, certain conclusions deserve mention. Since the ether molecule has no conformation which permits it a center of symmetry as required by the space group there must be pseudo-symmetry

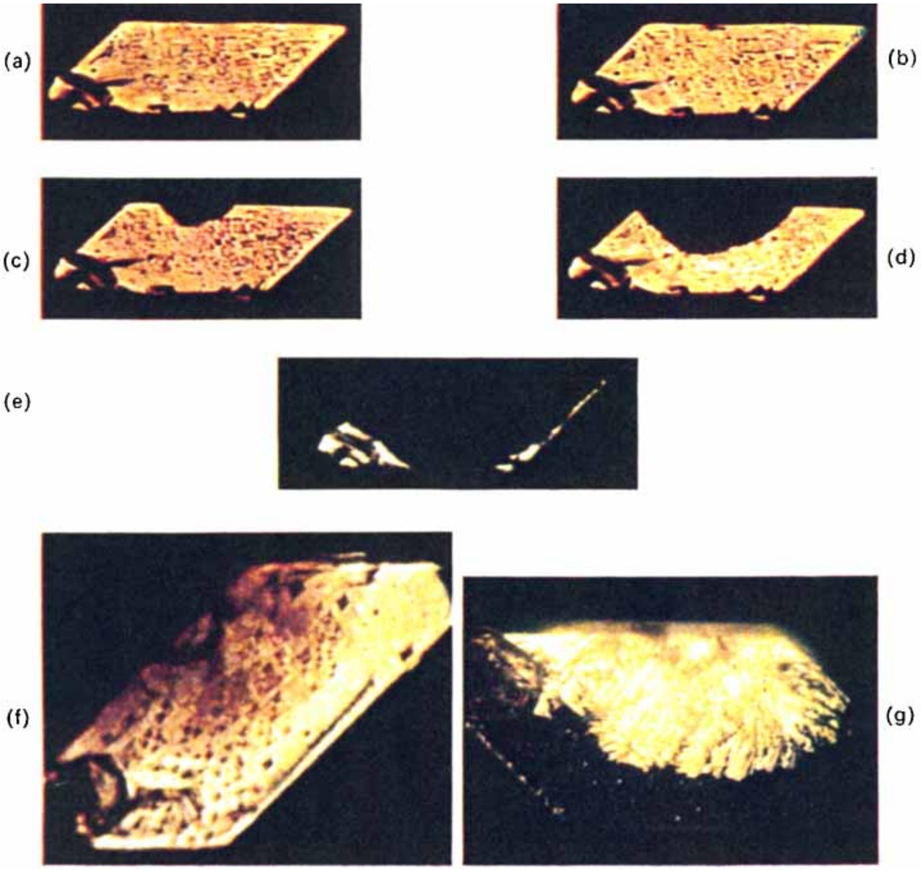

**Figure 2.** Loss of ether from the etherate of phenylazotribenzoylmethane etherate. (*a*) Crystal of etherate lying on an (010) face. (*b*) After 6 days at ambient temperature. (*c*) After 12 days. (*d*) After 20 days. (*e*) After 37 days. (*f*) Second crystal after 18 days. The crystal is oriented between crossed polaroids so that the unchanged region transmits light. (*g*) the same crystal as in (*f*) rotated to the extinction position for the unchanged part of the crystal.

resulting from disorder in the orientation of the ether molecules around the crystallographic centers.

The difference between the volume of the unit cell of the etherate (II) and that of the azo compound (I) (Table 1) is 308 Å$^3$. This result is in agreement with twice the value of 1305·Å$^3$ for the molecular volume estimated from the measured$^{(4)}$ density of crystalline diethyl ether at −195°.

Although few observations have been made of the manner in which small molecules are lost from crystals in which they are incorporated, the loss of water from a hydrate of phloroglucinol was observed$^{(5)}$ to have characteristics resembling the loss of ether from the etherate II. In each case solvent loss begins at an edge of the crystal and spreads in a direction parallel to the most highly developed faces of the crystal. In each case loss of solvent produces a crystal which retains its original shape but contains crystallites which scatter visible light, causing the crystal to appear opaque. Loss of ether from the etherate II has clearly not produced a new crystalline form of I. Although the gross structure is fragmented to a microcrystalline aggregate, the observation that a crystal of II after it has lost the incorporated ether but before it has been ground gives an X-ray " powder photograph " without broadening of the lines establishes an average value of 10$^3$ Å for the dimensions of the crystallites.$^{(6)}$ Results of the studies of the chemical reactivity of the de-etherated form of II will be reported elsewhere

## REFERENCES

1. Curtin, D. Y., Byrn, S. R. and Pendergrass, Jr., D. B., *J. Org. Chem.* **34,** 3345 (1969) and references cited therein.
2. Powell, H. M., " Non-stoichiometric Compounds," Ed. by L. Mandelcorn, Academic Press, New York, 1964, pp. 448 ff.
3. Puckett, R. T., Pfluger, C. E., and Curtin, D. Y., *J. Amer. Chem. Soc.* **88,** 4637 (1966).
4. Biltz, W., Fischer, W., Wünnenberg, E., *Zeit. Physik. Chem.* [A] **151,** 13 (1930).
5. Kofler, L. and Kofler, A., " Thermo-Mikro-Methoden zur Kennzeichnung Organischer Stoffe und Stoffgemishe, Verlag Chemie, GMBH, Weinheim/ Bergstrasse, 1954.

6. Stokes, A. R., " X-ray Diffraction by Polycrystalline Materials," Ed. by H. S. Peisser, H. P. Rooksby, and A. J. C. Wilson, Chapman and Hall, London, 1960, p. 409; Azaroff, L. V., and Buerger, M. J., " The Powder Method in X-ray Crystallography," McGraw-Hill Book Co., New York, N.Y., 1958, p. 254 ff.