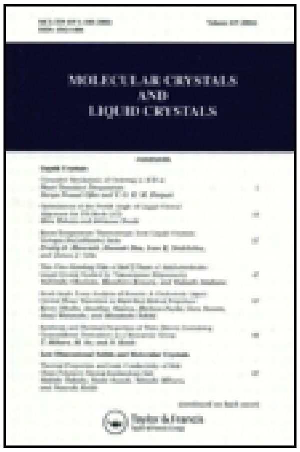

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Stephen K. Lower [a]

[a] Departement of Chemistry, Simon Fraser University, Burnaby 2, B.C., Canada

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Mixed-Donor Charge-Transfer Complexes: A New Type of Nonstoichiometric Compound[1]

STEPHEN K. LOWER

Department of Chemistry
Simon Fraser University
Burnaby 2, B.C., Canada

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Abstract—Crystalline complexes between aromatic hydrocarbon donors and trinitrobenzene which contain more than one species of donor molecule have been prepared. The system anthracene/phenanthrene-TNB is described in detail. The distinction between *solid solutions* and *compounds* as applied to charge-transfer complexes is discussed in terms of structural and energetic data; it is argued that mixed-donor complexes can be regarded as solid solutions when unexcited, and as non-stoichiometric compounds when excited to a polar charge-transfer state.

Introduction

Complexes between aromatic electron donors, particularly hydrocarbons, and electron acceptors such as picric acid or 1, 3, 5-trinitrobenzene (TNB) have long been known; their distinctive colors, melting points and crystalline forms have found application in characterizing a wide variety of aromatic substances. The stoichiometry of charge-transfer complexes is most commonly based on a 1 : 1 ratio of donor to acceptor molecules; the ratios 1 : 2 and 2 : 1 are also sometimes encountered, while other ratios are comparatively rare. A very few donor-acceptor combinations are known to form both 1 : 1 and 1 : 2 complexes.[2] These distinct ratios apply to complexes both in the crystalline state and in solution, although a given donor-acceptor combination may demonstrate different stoichiometries in the two states.[3]

Although the overall donor-to-acceptor ratio is constant for any given complex, we have observed that it is possible to prepare crystalline complexes in which more than one species of donor molecule is present, and in which the ratio of $donor_1$ to $donor_2$ can vary continuously over a wide range. For example, if phenanthrene-TNB (1 : 1) is recrystallized from solutions containing small amounts of anthracene-TNB (1 : 1), a series of crystals varying in color from pale yellow to orange can be isolated. The range of compositions that can be obtained by this method is limited by the constraints that the relative solubilities of the components place on the composition of the crystalline products.[4] A much wider range of $donor_1$-$donor_2$ ratios can be obtained by preparing melts of powdered mixtures containing known ratios of the parent complexes. These melts are most conveniently prepared and observed between microscope cover glasses. In this way a complete series of anthracene/phenanthrene-TNB complexes has been prepared, ranging in composition from 1 mole-% anthracene-TNB to 95 mole-% anthracene-TNB. The crystalline samples appear to be of entirely uniform composition under the polarizing microscope, showing the strong dichroism and parallel extinction that characterize the parent complexes. X-ray powder photography reveals the presence of only one crystal species except within the anthracene-TNB concentration range of 60-80 mole-%, where melting point data confirm that two phases are present. At anthracene-TNB concentrations up to about 60 mole-%, the crystal structure is clearly that of phenanthrene-TNB, while photographs of melts containing more than 80% anthracene-TNB correspond to the powder pattern of pure anthracene-TNB. Photographs of melts of the 60-80% region are similar to those of unmelted mixtures of the two parent complexes.

The melting-point composition diagram (Fig. 1) is indicative of the formation of two series of solid solutions, based respectively on the two parent complex lattices. The eutectic at 141 °C and the X-ray data indicate the region of immiscibility of the two solid solutions at room temperature and at the melting point. The solid-solid phase boundary shown on the diagram exists in pure phenanthrene-TNB; it is evidenced on the hot stage microscope by a rapid transition from the fairly uniform crystalline film initially formed on cooling, to a much more disordered morphology.

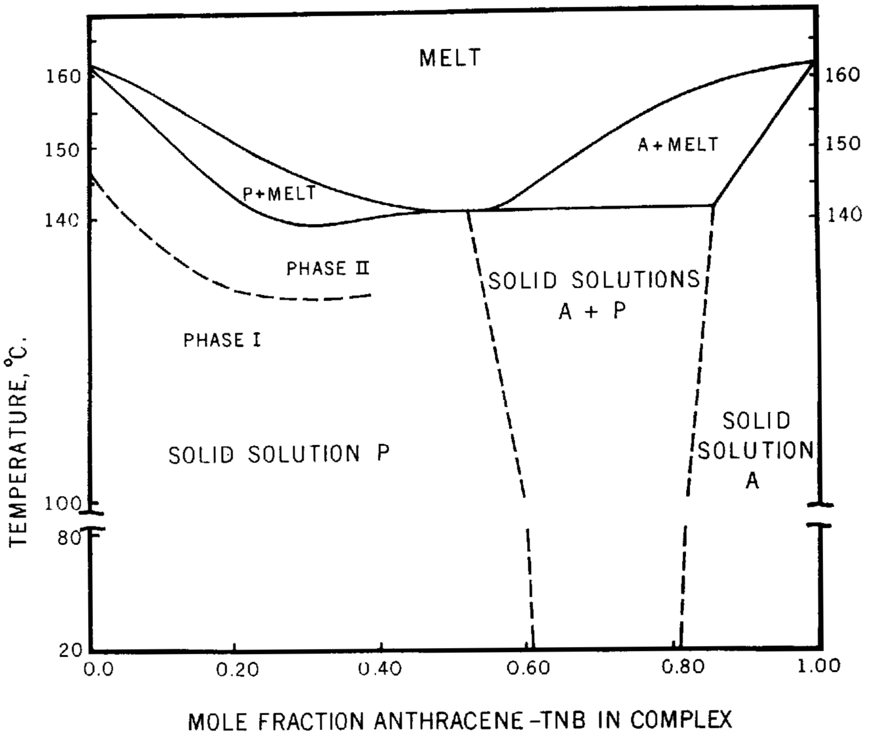

Figure 1. Melting point-composition diagram of the anthracene/phenanthrene-TNB system. Solid phases *P* and *A* show X-ray powder patterns identical to those of pure phenanthrene-TNB and pure anthracene-TNB, respectively. The two phases of solid *P* could not be distinguished at anthracene-TNB concentrations exceeding 40 mole-%.

Other series of mixed complexes have also been prepared, including phenthrene/azulene-TNB, perylene/pyrene-TNB, anthracene/acridine-TNB, and stilbene/azobenzene-TNB. Attempts to prepare mixed-acceptor complexes based on TNB/2, 4, 5, 7-tetranitro-9-fluorenone led to the formation of amorphous glasses rather than crystalline melts.

Experimental Notes

The anthracene and phenanthrene used were " scintillation grade ", Eastman X480 and X599, respectively (ordinary " pure " phenanthrene may contain up to 10% anthracene). The TNB complexes were prepared by dissolving each hydrocarbon together with the required amount of TNB (Eastman 639) in an appropriate[4] hot solvent (carbon tetrachloride for anthracene-TNB, methanol for phenanthrene-TNB). The crystals obtained on cooling were washed and recrystallized from the same solvent.

Solid mixtures were prepared by grinding together weighed portions of the two complexes in an agate mortar. A small portion of the powdered mixture was placed between microscope cover glasses and heated just above the melting point for 5–10 sec., then allowed to cool. Each sample was examined under a polarizing microscope to ensure that mixing was complete. Melting points and transition temperatures were determined on a Kofler hot stage, calibrated to within 1 °C.

Powdered samples for X-ray examination were placed in capillary tubes, melted, and cooled rapidly to promote maximum polycrystallinity. Chromium radiation was used with a vanadium filter.

Discussion

Whether these mixed-donor complexes can properly be regarded as nonstoichiometric *compounds* or are merely solid solutions of two distinct complexes must necessarily depend upon one's conception of the term " compound " when applied to a crystalline charge transfer complex. The crystal structure of phenanthrene-TNB has not been reported, but it is very likely similar to that of anthracene-TNB[5] which is representative of a large number of similar complexes.[6,7] These complexes generally consist of donor and acceptor molecules arranged alternatively in continuous stacks, the planes of the aromatic rings being approximately perpendicular to the long axis of the stacks, which are in turn parallel to the *c* axis of the monoclinic cell and to the morphological long axis of the crystal. Owing to the stacked arrangement, individual donor-acceptor pairs are not distinguishable in the crystal. Although the distances between adjacent donor and acceptor ring planes tend to be slightly smaller than normal van der Waals separations in aromatic crystals, the small values of these deviations and the relative orientations of the donor and acceptor molecules suggest that charge transfer forces, if they exist in the crystal at all, exert a very minor effect on the crystal structure, compared to other interactions and to the general requirement for efficient packing. That charge-transfer forces contribute little to the stability of the crystalline complex is shown also by the small (– 0.1 to – 1 kcal) values of the enthalpy of formation of a number of solid hydrocarbon-TNB complexes from the crystalline components.[8]

From this it would appear that solid charge-transfer complex " compounds " do not have significantly greater stability than we would expect to find in a solid solution of two " non-complexing " molecules such as *trans*-stilbene and bibenzyl. Compared to ordinary solid solutions, these complexes are unique only in their definite donor-acceptor stoichiometry. This stoichiometry is probably imposed more by the trivial requirements of order and packing that would govern the structure of any molecular crystal composed of two kinds of molecular units differing in size and shape, rather than by any special attractive or energetic properties (usually implied by the term " compound ") of the donor-acceptor pair itself. Similar remarks have been made in connection with complexes in fluid solution,[9] and give rise to the question posed by Evans[10] in his discussion of inorganic defect structures, as to the exact meaning of the term *chemical compound.*

What has been said thus far applies to the solid charge-transfer complex in its ground electronic state. Charge-transfer complexes are characterized by an absorption band, frequently in the visible region of the spectrum, that leads to an intermolecularly excited state in which a partial electronic charge has been transferred from the donor to the acceptor molecule. In anthracene-TNB and similar complexes, this absorption is strongly polarized along the donor-acceptor stack,[11] giving rise to the well known dichroism of the crystals. Although charge-transfer forces may be of negligible effect in the unexcited crystal, they give rise to very strong donor-acceptor interactions in the polar excited state.[12] Indeed, fluorescence polarization studies suggest that the molecules in the excited region of the anthracene-TNB crystal are actually reoriented as a result of these forces.[13] It might thus be argued that the solid charge-transfer complex "compound" exists only in the excited state, the ground state consisting of a solid solution of the two "reactants". The crystal can be regarded as a kind of solid state exciplex[14] in which interaction is not localized between distinct donor-acceptor pairs (as is presumably the case in solution[15]), but extends over the entire excited region of the crystal. To the extent that one chooses to regard the boundaries of the complex compound as being similarly delimited, it would seem reasonable to classify a crystalline mixed-donor (or mixed acceptor-) complex as nonstoichiometric in the same sense as, for example, a mixed crystal of NaCl-AgCl, in which the two cations can be present in any mole ratio.

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