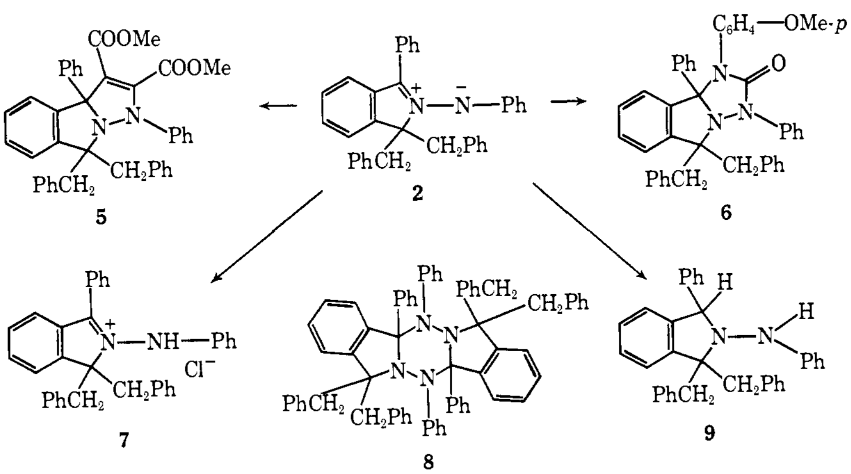


5

2

6

7

8

9

colorless adduct **5** (88%): mp 220–222°; ir (Nujol) 5.72 μ (ester C=O), 5.91 (ester C=O); $\lambda_{\max}^{CH_3CN}$ 332 mμ (ε 9400), 250 (8100). The nmr spectrum of **5** shows two AB quartets [**5**: nmr ($CDCl_3$) τ_A 7.31, τ_B 6.77 (q, 2 H, J_{AB} = 13.4 Hz, CH_2Ph), $\tau_{A'}$ 6.77, $\tau_{B'}$ 6.40 (q, 2 H, $J_{A'B'}$ = 12.6 Hz, CH_2Ph), τ 6.72 (s, 3 H, $COOCH_3$), 3.8–2.6 (m, 24 H, aromatic)], indicating that the two benzyl methylenes are no longer in an identical environment as would be expected from structure **5** for the adduct.

Similarly on gentle warming with *p*-methoxyphenyl isocyanate the photoisomer **2** yielded the adduct **6** (98%): mp 227–229°; ir (Nujol) 5.82 μ (C=O); $\lambda_{\max}^{CH_3CN}$ 255 mμ (ε 18,300); nmr ($CDCl_3$) τ_A 7.07, τ_B 6.66 (q, 2 H, J_{AB} = 14.0 Hz, CH_2Ph), $\tau_{A'}$ 6.73, $\tau_{B'}$ 6.51 (q, 2 H, $J_{A'B'}$ = 12.6 Hz, CH_2Ph), τ 6.40 (s, 3 H, OCH_3), 3.7–2.5 (m, 28 H, aromatic).

On exposure to gaseous hydrogen chloride, solutions of the photoisomer **2** furnished the crystalline yellow hydrochloride **7** (quantitative): mp 218–220° (decomposes to yield **2**); $\lambda_{\max}^{CH_3CN}$ 415 mμ (ε 3970), 284 (13,500); nmr ($CDCl_3$) 6.25 (s, sharp, 1 H, exchangeable with D, NH), τ_A 6.09, τ_B 5.37 (q, 4 H, J_{AB} = 13.4 Hz, two CH_2Ph groups), τ 3.5–2.0 (m, 24 H, aromatic).

That no skeletal rearrangement had occurred during treatment of **2** with hydrogen chloride was shown by the quantitative regeneration of **2** when **7** was treated with dilute aqueous alkali.

Attempts to methylate **2** with methyl iodide by refluxing in benzene solution for a prolonged period (2–3 days) were unsuccessful. Under these conditions the dimer **8** was isolated (45%) as yellow crystals: mp 235–237° (decomposes to **2**);[11] $\lambda_{\max}^{CH_3CN}$ 400 mμ (ε 5760), 290 (22,600), 245 (35,000); nmr ($CDCl_3$) τ_A 6.03, τ_B 5.35 (q, 8 H, J_{AB} = 14.0 Hz, four CH_2Ph groups), τ 3.3–2.3 (m, 48 H, aromatic).

In conformity with structure **2**, the photoisomer undergoes facile reduction with metal hydrides. Titration of ethanolic solutions of **2** with ethanolic sodium borohydride (the orange-red color of **2** serves as an indicator) at ambient temperatures results in the quantitative conversion to the colorless dihydro derivative **9**: mp 126–127°; nmr ($CDCl_3$) τ_A 6.78, τ_B 6.65 (q, 2 H, J_{AB} = 13.2 Hz), 5.52 (s, 1 H, CHPh), 4.74 (s, 1 H, exchangeable with D, NH), 3.7–2.6 (m, 24 H, aromatic).

Sensitization data suggest that the reaction **1** → **2** proceeds *via* the excited singlet state of **1**. Intervention of intermediates such as **3** or **4** in the photochemical reaction **1** → **2** cannot be excluded by the present data. Further studies are in progress and will form the subject of a future communication.

Acknowledgments. I wish to thank Dr. J. E. Lancaster for the nmr spectra and Drs. A. Zweig and A. K. Hoffmann for their valuable comments.

Balwant Singh
Central Research Division, American Cyanamid Company
Stamford, Connecticut 06904

Received March 28, 1969

Liquid-Crystal Polymorphism in Bis(4′-*n*-alkoxybenzal)-1,4-phenylenediamines

Sir:

We have found that bis(4′-*n*-alkoxybenzal)-1,4-phenylenediamine derivatives, in which the alkoxy chain lengths are C_5 to C_{18}, have a large number of first-order phase transitions. To our knowledge, no compound has been reported which has eight first-order phase transitions between condensed phases as observed in the case of C_7.

These dianils have been reported by Gray, *et al.*,[1] with only two liquid-crystal phases for those which have *n*-alkoxy chain lengths of C_5 to C_{12}, the higher temperature liquid-crystal phase being nematic and the lower one smectic. In the case of similar compounds with chain lengths C_{16} and C_{18}, only one smectic phase has been reported. Our observations of additional smectic phases with four of these compounds, prepared earlier for a comparison with the liquid-crystal phases of laterally substituted dianils,[2] encouraged us to prepare other homologs of the present series to investigate their liquid crystalline behavior.

Transition temperatures were determined by differential thermal analysis using a Du Pont DTA 900. The transitions with highest transition energy have been regarded as melting points (solid–liquid or solid–liquid-crystal transition). These transitions can be easily supercooled, whereas supercooling of liquid-crystal transitions is negligible. The assignments of the

---

(11) The dimer (tetrazine) dissociates into its monomer **2** on heating above its melting point (this was confirmed by spectral comparison of the melt with that of the pure compound **2**). The monomer–dimer equilibrium of this type has been observed previously (*cf.* ref 10).

(1) G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 4359 (1955).

(2) S. L. Arora, J. L. Fergason, and A. Saupe, Paper at the Liquid Crystal Conference, Kent, Ohio, 1968.

Table I. Bis-(4′-*n*-alkoxybenzal)-1,4-phenylenediamine

Substituents	Transition temperatures, °C, from solid or preceding liquid crystal state to: Smectic 5	Smectic 4	Smectic 3	Smectic 2	Smectic 1	Nematic	Isotropic
$C_5H_{11}O$						172, 171[b] (175),[a] 171.5[a,b]	264 271[a]
$C_6H_{13}O$		155	160	167	168 (169.5)[a]	187 189[a]	255 259.5[a]
$C_7H_{15}O$	125	148	155	161	168 (164.5)[a]	198 202.5[a]	240 245[a]
$C_8H_{17}O$	119	143	150	154	164 (160)[a]	203 209[a]	232 238[a]
$C_9H_{19}O$	120	145	148	149 (150.8)[a]	163	206 211.5[a]	223 228[a]
$C_{10}H_{21}O$	123	140	144	145 (145.5)[a]	163	208 212[a]	218 222[a]
$C_{12}H_{25}O$		122	131	134 (137.5)[a]	157	204 208[a]	205 209[a]
$C_{14}H_{29}O$		123	126	127	153		197
$C_{16}H_{33}O$				128 (127.5)[a]	149		189 191[a]
$C_{18}H_{37}O$				129 (135.5)[a]	147		183 187[a]

[a] Transition temperatures reported by Gray, *et al.*[1] Values in parentheses are the melting points reported by Gray, *et al.*[1] Many of these correspond to smectic–smectic transitions. [b] Transition from monotropic smectic.

transitions were confirmed by a Leitz Panphot polarizing microscope. The error of the temperature measurements is estimated to be less than ±2°.

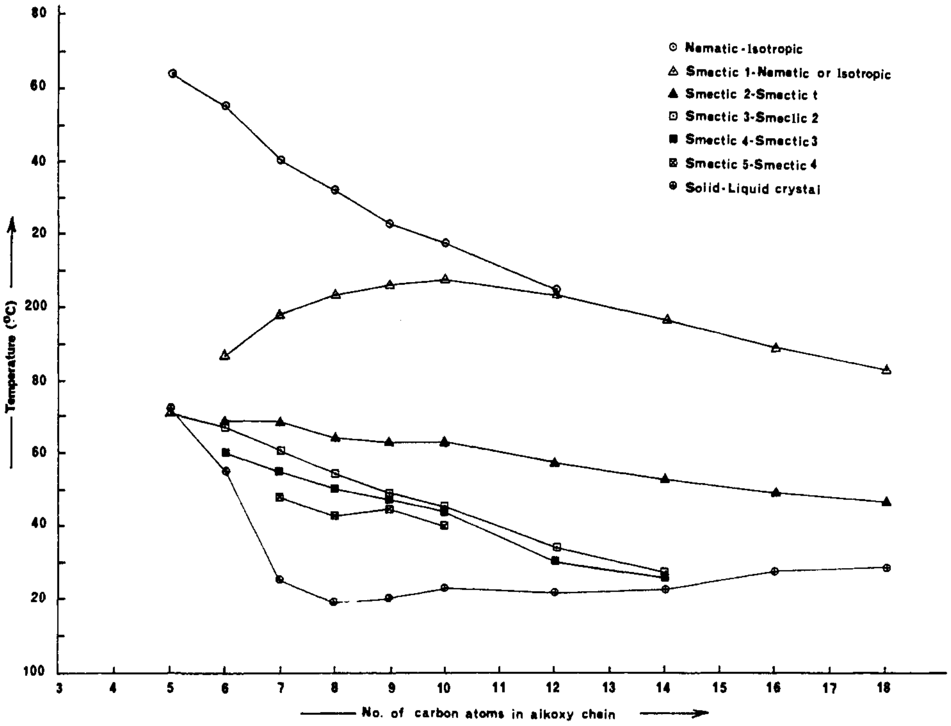


Figure 1.

However, an exception to the above generalization regarding temperatures as melting points was observed in the case of bis(4′-*n*-heptyloxybenzal)-1,4-phenylenediamine. In this case, on heating, differential thermal analysis showed first a transition at 115° with subsequent transitions at 125°, 148°, and other temperatures given in Table I. On cooling, all the higher temperature transitions were reversible with negligible supercooling except the ones observed at 125 and 115°. The transition at 125° could be supercooled usually by more than 5° and did not have the highest transition energy, in comparison to that observed at 115°, which could also be easily supercooled. Optical studies indicate that the phase between 115 and 125° is not observable by the microscopic studies on initial heating. However, on cooling below 125°, this phase retains a texture similar to a smectic mosaic texture, which exists until the material obviously crystallizes. The thin layer of the material in this phase did not flow when a shear stress was applied to the cover slide; it could possibly be a crystalline modification. At the present time, we do not have an explanation for this abnormal behavior. The transition temperatures for the various liquid crystal phases are listed in Table I. In this table and Figure 1 we followed the usual convention for the nomenclature of smectic phases. The highest temperature smectic phase is always called smectic 1, the next lower one smectic 2, and so on. In Figure 1, transition temperatures have been plotted and connecting curves have been drawn on the basis of optical texture.

The optical studies indicate that smectic 1 is identical with smectic C, with the exception of the C_5 in which smectic 1 shows a mosaic texture. Smectic 2 cannot readily be identified with one of the smectic phases A, B, or C as defined by Sackmann and Demus.[3] It is comparable in texture with smectic C but shows fewer discontinuities in the schlieren texture. Smectic 3 could correspond to smectic B (mosaic texture); smectic 4 and 5 have the same basic texture as smectic 3 but with increased discontinuities and spontaneous flow at the boundaries of the blocks. The flow is the greatest in smectic 5. These phases are observable with the polarizing microscope if thin sections of the materials are prepared. With thick sections, the smectic phases tend to assume a fan texture in which it is difficult to observe the transitions.

Some substances have been reported with up to three thermotropic smectic phases, and they have been thoroughly studied for the classification of these phases (see, for instance, ref 3 and 4). These dianils with an unusually large number of smectic phases, up to five or maybe even six, show that there exists additional phases that have not yet been classified. Further work on the classification of these phases on the basis of the miscibility with other liquid crystalline phases is in progress.

Acknowledgment. The research reported in this paper was sponsored by the Aerospace Medical Research Laboratories, Aerospace Medical Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract No. F-33615-67-C-1496 with Kent State University. This paper has been identified by Aerospace Medical Research Laboratories as AMRL-TR-69-33.

(3) H. Sackmann and D. Demus, *Mol. Crystals*, 2, 81 (1966).

(4) D. Demus, H. Sackmann, G. Kunicke, G. Pelzl, and R. Salffner, *Z. Naturforsch.*, 23a, 76 (1968).

Sardari L. Arora, Ted R. Taylor
James L. Fergason, Alfred Saupe
Liquid Crystal Institute
Kent State University, Kent, Ohio 44240

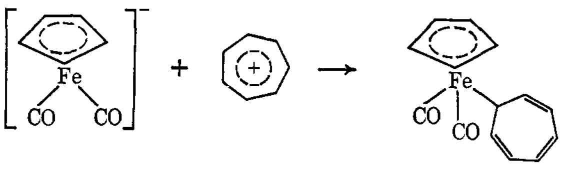
Received March 20, 1969

(7-*Monohapto*cycloheptatrienyl)-(*pentahapto*cyclopentadienyl)dicarbonyliron

Sir:

The class of fluxional organometallic complexes encompasses a number of *monohapto*[1] compounds all of which are h^1-cyclopentadienyl derivatives.[2] No complex having a transition metal similarly bonded to a cycloheptatriene ring is known. The purpose of the present communication is to report the preparation and properties of the first such complex, (7-*monohapto*cycloheptatrienyl)(*pentahapto*cyclopentadienyl)dicarbonyliron (**1**).

This substance is formed in 4% yield along with $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ and ditropyl when the anion $(h^5\text{-}C_5H_5)Fe(CO)_2^-$ is brought into reaction with tropylium tetrafluoroborate at −70° in tetrahydrofuran solution.



1

The complex, purified by column chromatography on alumina, is a red, crystalline material, mp 98–99°. Its general stability toward decomposition both in the solid state and in solution appears to be greater than the closely related *monohapto*cyclopentadienyl complex $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)Fe(CO)_2$ (**2**).[3] Thus **1** is moderately stable in the air in the crystalline state and can be kept for prolonged periods in degassed solutions at 0°. It is, however, rapidly decomposed in hydroxylic media and when its otherwise stable organic solutions are exposed to air.

Its infrared spectrum, taken in $CHCl_3$, exhibits only a single broad carbonyl absorption at 1930 cm^{-1}, but in CCl_4 solution this is split into two sharp peaks at 2055 and 2010 cm^{-1} and a broad intense peak at 1920 cm^{-1}. In CS_2 solution the compound has peaks at 3020, 3007, 1925, 1890 (sh), 1416, 1010, 990, 887, 842, 831, 820, 705, 610, 577, and 525 cm^{-1}.

In conformity with structure **1**, the mass spectrum of the complex has intense peaks at *m/e* 268 (molecular ion) and at 240 and 212, corresponding to the loss of one and two carbonyl groups, respectively, from the parent ion. Other intense peaks occur at *m/e* 147 ($C_7H_7Fe^+$), 121 ($C_5H_5Fe^+$), 91 ($C_7H_7^+$), and 56 (Fe^+).

The temperature dependence of the nmr spectrum of **1** is typical of fluxional molecules. At 30°, the spectrum, taken in deuteriotoluene solution, consists of a sharp singlet at δ 4.1 and a broad absorption (width at half-height ~18 Hz) centered at δ 4.8, with relative areas of 5:7. These absorptions are assigned to cyclopentadienyl and cycloheptatrienyl protons, respectively. As the temperature is lowered, the cyclopentadienyl peak remains unchanged in aspect while the cycloheptatrienyl peak broadens further and is finally decomposed at about −15° into four broad absorptions. At −50° these appear as four well-defined complex absorptions of relative area 2:2:2:1, comprising a broad, unresolved multiplet centered at δ 6.05, a well-defined six-line multiplet centered at δ 5.20,[4] a

---

(1) The nomenclature used is that recently suggested by F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).

(2) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966); F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967); G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967); H. B. Fritz and G. G. Kreiter, *J. Organometal. Chem.*, **4**, 313 (1965); A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968); E. Maslowsky and K. Nakamoto, *Chem. Commun.*, 257 (1968).

(3) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 3, 104 (1956); B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

(4) Analysis of this multiplet as an AA′XX′ set ($H_{2,3,4,5}$) with $J_{2,5}$ = 0 Hz leads to the following values for the coupling constants: $J_{3,4}$ = 7.5, $J_{2,3}$ = 11.2, and $J_{2,4}$ = 1.1 Hz. These values compare closely with those reported recently for cycloheptatriene by J. B. Lambert, L. J. Durham, P. Lepoutre, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3986 (1965): $J_{3,4}$ = 10.67, $J_{2,3}$ = 5.26, $J_{2,4}$ = 0.80 Hz.