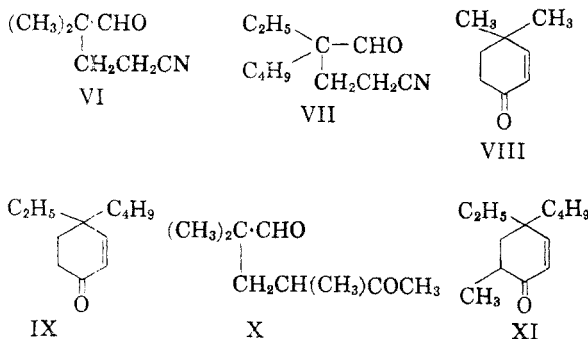ethanol), m.p. 142°. *Anal.* Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3. Found: C, 55.4; H, 5.7. [aa] Diluted with 30 ml. of methanol. [bb] Anal. Calcd. for $C_{12}H_{20}O$: C, 80.0; H, 11.1. Found: C, 79.3; H, 10.9. n_D^{15} 1.4885; d_4^{15} 0.9313. MR, calcd., 55.20; MR, found, 55.70. ν_{max}^{liq} 1695 cm.$^{-1}$ (carbonyl). [cc] 2,4-Dinitrophenylhydrazone, orange-red platelets, (from isopropanol), m.p. 100°. *Anal.* Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.9; H, 6.7. Found, C, 60.6 H. 6.9. [dd] n_D^{20} 1.4593; d_4^{20} 0.9734. MR, calcd., 44.04; found, 44.30. ν_{max}^{liq} 1700 and 1720 cm.$^{-1}$ The 2,4-dinitrophenylhydrazone is yellow. The analysis is not satisfactory; the distillation is probably accompanied by partial cyclization. *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 70.7; H, 9.8. [ee] n_D^{15} 1.4800; d_4^{20} 0.9295. MR, Calcd., 59.77; MR, found, 59.40. ν_{max}^{liq} 1700 cm.$^{-1}$ The 2,4-dinitrophenylhydrazone is red.

Analogously, VII[10] has been obtained from 2-ethylhexanal and acrylonitrile. With methyl vinyl ketone, a smooth reaction took place, which was accompanied by spontaneous ring formation and led to 4,4-dimethylcyclohex-2-en-1-one (VIII) and 4-butyl-4-ethylcyclohex-2-en-1-one (IX), respectively. These formulas are suggested by the molecular refraction, the infrared spectrum, and the red color of the 2,4-dinitrophenylhydrazones. In the reaction with aldehydes, too, methyl isopropenyl ketone tended to give open-chain products. At least

with isobutyraldehyde, 2,2,4-trimethyl-5-oxohexanal (X) was obtained, as evidenced by the infrared spectrum, the molecular refraction and the yellow color of the 2,4-dinitrophenylhydrazone, while with 2-ethylhexanal, 4-butyl-4-ethyl-6-methylcyclohex-2-en-1-one (XI) was formed. The experiments are summarized in Table III.

In conclusion, it is reported that the following systems could not be induced to react under the influence of basic resins: *methyl methacrylate* with diethyl malonate, benzyl cyanide, or isobutyraldehyde; *ethyl crotonate* with ethyl acetoacetate, diethyl malonate, benzyl cyanide, or isobutyraldehyde; *acrylonitrile* with ethyl hippurate or acetophenone; *ethyl cinnamate* with 2-nitropropane, benzyl cyanide, or ethyl acetoacetate, *ethyl cinnamylideneacetate* with 2-nitropropane; *cinnamaldehyde* with 2-nitropropane or ethyl acetoacetate; *crotonaldehyde* with isobutyraldehyde or methyl ethyl ketone, *benzylideneacetone* with cyclopentanone or 2-carbethoxycyclopentanone.[11]

TEL-AVIV, ISRAEL

(10) H. A. Bruson and W. D. Niederhauser, U. S. Patent 2,437,906 [*Chem. Abstr.*, 42, 4196 (1948)] obtained this compound from 2-ethylhexanal and β-hydroxypropionitrile, Mastagli *et al.*,[3] by the method described here.

(11) It may, of course, be possible that under conditions different from those employed by us, at least some of these reactions will take place. Details of the negative experiments are to be found in the Ph.D. thesis of R. Corett, submitted to the Senate of the Hebrew University, Jerusalem.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

A Molecular Compound between Benzene and trans-9,10-Di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol

EMIL J. MORICONI, FRIEDRICH T. WALLENBERGER, AND WILLIAM F. O'CONNOR

Benzene and *trans*-9,10-di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol (trans-II) form a 1:1 molecular compound (I) which has been characterized by thermogravimetric analysis, and quantitative removal and identification of the benzene moiety. The firm retention of benzene in I and its release in various solvents suggests a monomolecular inclusion type compound (III).

The literature[1] records over one hundred binary molecular compounds containing benzene (0.25–4 moles) and a second organic constituent (1–4 moles).[2] Three of these, all diols, involve binary mo-

lecular compound formation of benzene with only one of two possible geometric isomers: *trans*-5,12-dihydro-5,6,11,12-tetraphenyl-5,12-naphthacene-diol,[23] *cis*-3,4-dihydroxy-3,4-diphenyl-1,1-cyclopen-

(1) *Chemical Abstracts* covered to end of 1956.

(2) In most cases, molecular composition has been deduced from carbon-hydrogen analyses. Other more precise methods which have been used for the characterization of these benzene-containing molecular compounds include [second organic compound in parenthesis]: (a) Melting point diagrams of binary systems [CCl₄,[3,4,5] CBr₄,[4,5]

CI₄,[4] 1,3,5-trinitrobenzene,[6,7a] picric acid,[7b] and picryl chloride[7a,8]]; (b) Weight loss after heating *in vacuo* [picryl chloride,[6] 1,3,5-trinitrobenzene,[8] octaphenyltetrasiloxane,[9a] 6-chloro-2,3-bis(p-chloranilino)quinoxaline,[10] heptabenzoyl-streptidine,[11] tris(triphenylgermyl)silyl bromide[12] and tris-(triphenylgermyl)silol[12]]. The benzene stripped off on heating *in vacuo* has been caught in a trap and weighed,[12] and identified by its m.p.,[12] determined colorimetrically[9a] or

tanedicarboxylic acid,[24] and cis-1-(3,4-dimethoxy-phenyl) - 1,2,3,4 - tetrahydro - 6,7 - dimethoxy - 2,3 - naphthalenedimethanol.[25] Benzene also forms molecular compounds with (+) and (−)1,2,2,2-tet-raphenylethyl ₅hydrogen phthalate but shows no tendency to complex with the racemate.[26] By con-

spectrophotometrically.[9b] Benzene has also been condensed onto the solvent-free organic moiety and the combined benzene redetermined by weight loss[12]; (c) X-ray diffraction [octaphenylcyclotetrasiloxane,[9a] tri-o-thymotide,[13,14] and p-2,2,4-trimethyl-4-chromanylphenol[15,16]]; (d) Spectrophoto-metric [oxalyl chloride,[17,18] 1,3,5-trinitrobenzene,[18,19] maleic anhydride,[20a,20b] chloromaleic anhydride,[20b] benzoquinone,[20b] and tetranitromethane[21]]; and (e) Measuring the change in distribution ratio of picric acid between solvent $CHCl_3$ and water, when benzene is added to the solvent.[22]

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(9) (a) J. F. Hyde, L. K. Frevel, H. S. Nutting, P. S. Petrie, and M. A. Purcell, J. Am. Chem. Soc., 69, 488 (1947). (b) W. R. Nes, J. Am. Chem. Soc., 78, 193 (1956).

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(14) A. C. D. Newman and H. M. Powell, J. Chem. Soc., 3747 (1952).

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(18) H. McConnell, J. S. Ham, and J. R. Platt, J. Chem. Phys., 21, 66 (1953).

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(21) M. T. Robers, American Chemical Society Division of Petroleum Chemistry, General Papers No. 33, 5 (1955); Chem. Abstr., 50, 12455 (1956).

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(23) C. Dufraisse and L. Veluz, Bull. soc. chim. France [5], 3, 1905 (1936). The trans-configuration is our assignment. Dufraisse and Veluz prepared this compound by the addition of a tenfold excess of PhMgBr to 6,11-diphenyl-5,12-naphthacenequinone.

(24) E. Larsson, Trans. Chalmers Univ. Technol., Gothen-burg, No. 51, 19 (1946); Chem. Abstr., 41, 4460 (1947).

(25) M. E. Cisney, W. L. Shilling, W. M. Hearon, and D. W. Goheen, J. Am. Chem. Soc., 76, 5083 (1954).

(26) L. Ellison and J. Kenyon, J. Chem. Soc., 779 (1954).

trast, Newman and Powell[14] have found self-resolu-tion to be induced in the crystallization of inactive (±) tri-o-thymotide with benzene to yield an opti-cally active diastereomeric molecular compound.

In a previous paper,[27] we reported the isolation of a low melting adduct, m.p. 103–104°, (I) between trans-9,10-di(p-tolyl)-9,10-dihydro-9,10-phenan-threnediol (trans-II), m.p. 140–142° and recrystal-lizing solvent benzene. The adduct was tentatively identified by its infrared spectrum in CS_2 and CCl_4
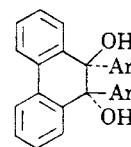
trans-II; Ar = p-tolyl

which was virtually superimposable upon that of trans-II with the single exception of a strong ben-zene band at 14.82 microns.[28] The infrared spectra in benzene were identical.

This paper reports further on the properties of this molecular compound (I) between trans-II diol and benzene and suggests a possible structure for I.

We have found that both I and trans-II absorb maximally in the ultraviolet region at 278 mμ, log $\epsilon_{max}^{cyclohexane}$ (I), 4.11; log $\epsilon_{max}^{cyclohexane}$ (trans-II), 4.13. Combustion analyses indicated a 1:1 molar ratio.[29] trans-II exhibits a remarkable specificity for ben-zene in molecular compound formation. Trans-II and I have been recrystallized from some twenty-two different solvents: benzene, toluene, m- and p-xylene, mesitylene, anisole, aniline, nitrobenzene, pyridine,[30] dioxane, cyclohexane, furan, thiophene, methanol, ethanol, ethanol-benzene, 1-propanol, 2-propanol, 1-pentanol, acetone, acetic acid, and car-bon tetrachloride. Trans-II was recovered from all solvents except benzene which gave I. All solvents except benzene converted I to trans-II.[31] In ben-zene, I was recovered unchanged. It is pertinent to note that neither cis-II diol nor any other of the cis- and trans-diols in the series previously re-

(27) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn, and W. F. O'Connor, J. Org. Chem., 22, 1656 (1957).

(28) We are indebted to Dr. R. L. Wagner, Chas. Pfizer and Co., Inc., for the infrared (CS_2) and ultraviolet (cyclo-hexane) solution spectra of these compounds.

(29) W. E. Bachmann [J. Am. Chem. Soc., 54, 1969 (1932)] has reported the preparation of I, m.p. 103°, from benzene-alcohol as a "modification" of the low-melting isomer, trans-II, m.p. 136°, but recorded combustion analyses only of trans-II. He noted that the melting point of I remained unchanged on recrystallization from ethanol (at variance with our results), and that both "modifica-tions" behaved alike on oxidation and rearrangement.

(30) Trans-II in pyridine forms beautiful, initially trans-parent, large hexagonal crystals which slowly lose pyridine on standing in air. The pyridine is completely removed on drying in a pistol at 58°/2–3 mm. for 48 hr.

(31) This behavior suggests that I in solution acts as a mixture of trans-II and benzene. Thus absorption spectra of I in CCl_4 and cyclohexane would merely indicate the presence of benzene.
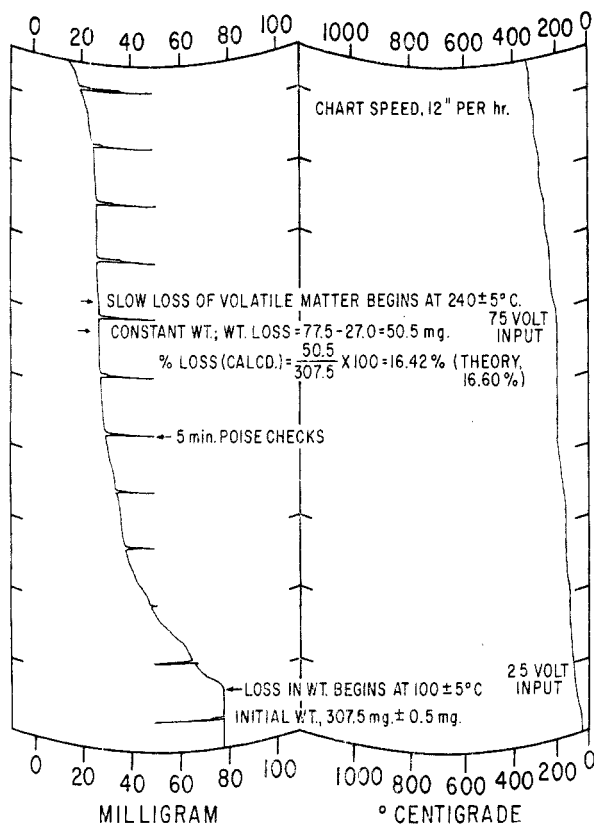
Fig. 1. Thermobalance record: ignition of molecular compound (I) composed of trans-9,10-di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol (trans-II) and benzene in a 1:1 mole ratio

Fig. 2. Thermobalance record: ignition of trans-9,10-di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol (trans-II)

ported[27] exhibited similar behavior in benzene. Further, cis- and trans-1,2-di(p-tolyl)acenaphthenediols also do not form molecular compounds with benzene.[32]

I is quite stable. Its melting point remained unchanged on heating in a drying pistol (acetone reflux), 58°/2–3 mm. for 48 hr. Thermogravimetric analysis[33] (Fig. 1) indicates that benzene is quantitatively stripped off at a temperature commencing at 100 ± 5°, with no further volatilization of the residue until 240 ± 5° (cf. Fig. 2). Distillation of I (1.000 g.) also gave at 105–108°/759 mm., a quantitative recovery of benzene (0.163 g.; theory, 0.166 g.), identified by boiling point and conversion to m-dinitrobenzene, m.p. 88–89°.[34] A sample of I, on standing in a closed vial at ambient temperatures for over two years showed a 50% loss of benzene.

The 1:1 molar ratio, the firm retention of benzene in I and its release in various solvents suggest the

possibility of what Powell[35,36] has classified as a monomolecular inclusion compound.[37] Unlikely alternatives include chemical interaction (covalent bond), electrostatic interaction (π bond, H-bond) arising from the polarization of one component by another in the solid state relative to the solution,[38]

(35) H. M. Powell, J. Chem. Soc., 61 (1948).

(36) H. M. Powell, Endeavour, 9, 154 (1950).

(37) Similar to that proposed by: F. Cramer in Einschlussverbindungen, J. Springer Verlag, Berlin, Germany, 115 pp., and Angew. Chem., 68, 115 (1956) for the cyclodextrins [K. Freudenberg and R. Jacobi, Ann., 518, 102 (1935); D. French and R. E. Rundle, J. Am. Chem. Soc., 64, 1651 (1942); K. Freudenberg and F. Cramer, Ber., 83, 296 (1950)]; and H. Stetter and E. E. Roos, Ber., 88, 1390 (1955) for several bis-N,N'-alkylenebenzidines.

(38) The only significant polar groups in trans-II are the two OH groups on adjacent, bridge carbon atoms. The two possible skew conformations for trans-II show both OH groups as axial (i) or equatorial (ii).

Intramolecular hydrogen bonding measurements[27] on trans-II show only a free OH absorption frequency at 3552 cm.[-1] suggesting conformation (i) in the ground state. I in CCl₄ also absorbs at 3552 cm.[-1] corresponding to a free OH stretching frequency.[39,40] The data at least indicate no measureable concentration of molecules at equilibrium having two equatorial OH groups of the probable conformation (ii).

(32) E. J. Moriconi, F. T. Wallenberger, E. A. Keneally, and W. F. O'Connor, unpublished results.

(33) We are grateful to Dr. Michael Cefola, Fordham University, for the use of the thermobalance, and to the Rev. Alfred Celiano for the determinations.

(34) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, The Systematic Identification of Organic Compounds, John Wiley and Sons, Inc., New York, N. Y., 4th ed., 1956, p. 323.
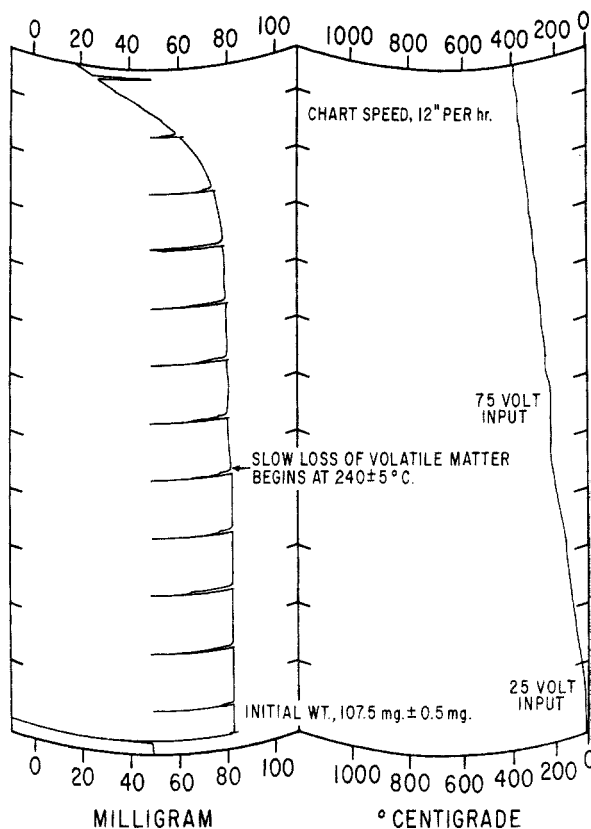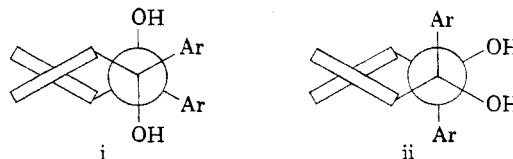
and electron-donor:electron-acceptor complexes.[41]

Monomolecular inclusion compounds however hold the enclosed guest molecule in a cage-like space in the center of the host component without the formation of any additional bonding other than the normally weak van der Waals forces.[35-37] A possible structural arrangement for I is suggested in III where the benzene moiety is confined between the equatorial p-tolyl substituents. The p-methyl groups accomplish a "locking effect" comparable to the caging effect of a cyclic host component.

III
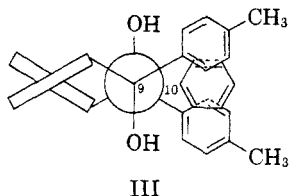
EXPERIMENTAL

Melting points are uncorrected. The microanalyses were performed by Dr. F. B. Strauss and Dr. G. Weiler Microanalytical Laboratory, Mr. J. Alicino, E. R. Squibb and Sons, New Brunswick, N. J., and Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Hydroxyl absorption measurements were made with a Perkin-Elmer Model

(39) See however ref. 31.
(40) We are indebted to Dr. Lester P. Kuhn, Ballistics Research Laboratory, Aberdeen Proving Ground, Md., for these infrared measurements.
(41) Although benzene can be considered a weak electron donor, there should be little difference between $trans$-II and cis-II diols as electron acceptors. Yet the latter does not form a molecular compound with benzene. Further, the electron acceptor complexes with benzene involve such electronegative atoms, groups, and molecules as the halogens,[3-5] nitro groups,[6-8,18,19,21] oxalyl chloride,[17,18] and dienophiles.[20] A general discussion of molecular complexes of this type, and theories as to the precise nature of the union between electron-attracting compounds and aromatics is available in G. M. Badger, $The\ Structures\ and\ Reactions\ of\ the\ Aromatic\ Compounds$, University Press, Cambridge, 1954, pp. 79–87.

12 B spectrometer equipped with a LiF prism; concn., 10 mg./ml., cell thickness, 0.1 mm., $CHCl_3$ solvent.[40] Thermoanalytical data were obtained with a Stanton milligram thermobalance.[33]

$trans$-9,10-Di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol ($trans$-II), m.p. 140–142°.[27]

Molecular compound (I), m.p. 103–104°, was obtained simply by recrystallizing $trans$-II from warm benzene.

$Anal.$ Calcd. for $C_{28}H_{24}O_2{:}C_6H_6$: C, 86.77; H, 6.43. Mol. wt. 470. Found: C, 86.63; H, 6.52. Mol. wt., 232, 268.[42] A mixed m.p. of $trans$-II and I is depressed.

I (2-$yr.\ old\ sample$).

$Anal.$ Calcd. for $C_{28}H_{24}O_2{:}05C_6H_6$: C, 86.28; H, 6.30. Found: C, 86.02; H, 6.39.

$Recrystallizing\ solvent\ study.$ Approximately 100 mg. of I or $trans$-II was dissolved in the minimum amount of boiling solvent. If a solid had not crystallized after cooling within 24 hr., the solvent was removed $in\ vacuo$, and the m.p. of the residue was taken. The m.p. of $trans$-II from all solvents except benzene ranged from 138 to 141°.

$Microdistillation\ of$ I. One g. of I was slowly heated at atmospheric pressure in a microdistillation flask of conventional design. At 102–104°, I melted and almost simultaneously the benzene was distilled (105–108°) and collected into a previously weighed side arm trap immersed in a Dry Ice-acetone bath.

m-$Dinitrobenzene.$ The benzene distillate was added to 1 ml. of conc. H_2SO_4 followed by dropwise addition of 1 ml. of conc. HNO_3 with vigorous stirring. After cooling the test tube in a beaker of water, the acid solution was poured onto 20 g. of ice. The precipitate was collected on a filter and recrystallized from alcohol, m.p. 88–89°[34]; admixture of the latter with an authentic sample showed no depression.

(42) Rast molecular weights in camphor for these molecular compounds are generally low.[9]

Pyrroles. XIII. Structure and Reactivity of N-Methyl-2-pyrrolealdehyde[1]

WERNER HERZ AND JAY BRASCH[2]

On the basis of its similarity to 2-pyrrolealdehyde in chemical behavior and physical properties, N-methyl-2-pyrrolealdehyde is assigned a structure to which a dipolar form contributes materially.

A number of explanations have been advanced to account for the physical properties of 2-pyrrolealde-

(1) Paper XII. W. Herz and J. Brasch, $J.\ Org.\ Chem.$, **23**, 711 (1958). This work was supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-01-009-ORD-436.

hyde and to explain its failure to undergo many of the ordinary aldehyde reactions.[3,4] There seems to

(2) Abstracted from the M.S. thesis of Jay Brasch, August 1957.