Since the dispersion of both the refractivity and the Verdet constant is governed by the term $\Sigma A_i/(\nu_i^2 - \nu^2)$, constancy of the ratio $\Delta V/\Delta n$ would be indicative of the fact that the electronic transitions responsible for both are identical. The data in the last column show that this expectation is essentially fulfilled, as has also been found for various aliphatic oxygen compounds.[8]

(8) W. J. Lewis and E. J. Evans, *Phil. Mag.*, **13**, 265 (1932).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIF. RECEIVED MAY 24, 1948

The Cryoscopic Behavior of 1,1-Dimethylcyclohexane Containing Certain Hydrocarbon Impurities[1]

BY G. L. EVANS,[2] K. W. GREENLEE, J. M. DERFER AND C. E. BOORD

A short investigation has been made concerning the cryoscopic behavior of 1,1-dimethylcyclohexane upon introduction of certain selected hydrocarbon impurities. This study was prompted by the observation that introduction of a small amount of *cis*-1,2-dimethylcyclohexane as an impurity in 1,1-dimethylcyclohexane caused an increase in the freezing point of the latter hydrocarbon, instead of the normal lowering. Although similar irregularities caused by solid solution formation have been observed in several binary hydrocarbon systems studied in detail by other workers,[3,4,5,6] it was thought that this new information would prove helpful because of the widespread reliance on cryoscopic data as criteria of purity.

The results of this investigation are summarized in Table I.

It will be noted that of the solutes used only *n*-heptane and *n*-butylcyclohexane produced normal freezing point lowering; *cis*-1,2-dimethylcyclohexane actually raised the freezing point, and the remaining solutes caused only a fraction of the normal lowering. In every case of abnormal behavior the apparent purity as calculated from the freezing point data was, of course, too high.

TABLE I

CRYOSCOPIC BEHAVIOR OF 1,1-DIMETHYLCYCLOHEXANE CONTAINING HYDROCARBON IMPURITIES

Solute (impurity)	Total mole % impurity added	Freezing point (°C.)	Observed Δt (°C.)	Expected[a] Δt (°C.)	Actual purity[b] (mole %)	Apparent purity[a] (mole %)
None added	0	−35.83 ± 0.04	....	....	99.04	...
cis-1,2-Dimethylcyclohexane	0.931	−35.66 ± .05	+0.17	−2.25	98.11	99.11
	1.97	−35.42 ± .07	+0.41	−4.79	97.07	99.21
None added	0	−35.52 ± .04	....	....	99.17	...
trans-1,2-Dimethylcyclohexane	0.648	−35.58 ± .04	−0.06	−1.57	98.52	99.15
	1.33	−35.69 ± .06	−0.17	−3.22	97.84	99.10
None added	0	−36.21 ± .03	....	....	98.88	...
trans-1,4-Dimethylcyclohexane	0.676	−37.23 ± .02	−1.02	−1.66	98.20	98.46
	1.35	−38.39 ± .05	−2.18	−3.29	97.53	97.98
None added	0	−35.64 ± .02	....	....	99.12	...
Cyclohexane	1.26	−36.44 ± .04	−0.80	−3.05	97.86	98.79
	2.30	−37.09 ± .03	−1.45	−5.59	96.82	98.52
None added	0	−35.79 ± .03	....	....	99.06	...
2,2,3-Trimethylbutane	0.671	−35.97 ± .03	−0.18	−1.62	98.39	98.98
	1.59	−36.10 ± .05	−0.31	−3.85	97.47	98.93
None added	0	−35.58 ± .04	....	....	99.15	...
n-Heptane	0.798	−37.49 ± .02	−1.91	−1.92	98.35	98.36
	1.19	−38.36 ± .02	−2.78	−2.87	97.96	98.00
None added	0	−35.74 ± .05	....	....	99.08	...
n-Butylcyclohexane	0.643	−37.25 ± .05	−1.51	−1.54	98.44	98.45
	1.04	−38.23 ± .04	−2.49	−2.52	98.04	98.05

[a] These data were calculated from the approximate equation $\log_{10} p = 2 - (A/2.303)(t_{f_0} - t_f)$ where p = purity (actual or apparent) in mole per cent., t_{f_0} = freezing point at 100% purity t_f = experimental freezing point (actual or expected) and $A = \Delta H^\circ_m/RT_{f_0}$ in which ΔH°_m is the heat of fusion (per mole). Values for t_{f_0} (−33.54°) and A (0.0042 deg.$^{-1}$) had been given by the American Petroleum Institute Research Project 44 in Selected Values of Properties of Hydrocarbons (Circular of the National Bureau of Standards C461) Table 7z. [b] The original purity of each sample was calculated from its freezing point using the equation and data mentioned in footnote *a*, assuming that no impurity leading to abnormal behavior was already present. The subsequent (lower) purities were obtained from the original purities by subtracting the mole percentages of impurity added.

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[3] Smittenberg, Hoog and Henkes, THIS JOURNAL, **60**, 17 (1938).

[4] Took and Aston, *ibid.*, **67**, 2275 (1945).

[5] Fink, Cines, Frey and Aston, *ibid.*, **69**, 1501 (1947).

[6] Hirschler, King and Faulconer, paper presented before the Petroleum Division at the Chicago, Illinois, meeting of the American Chemical Society, April, 1948.

The ability to form mixed crystals (solid solutions) is common to all hydrocarbons having low heats and entropies of fusion, as has 1,1-dimethylcyclohexane. Such molecules rotate in the solid phase below their melting points and possess considerable mobility of structure, enabling solute molecules of similar size and shape to be accommodated in the crystal lattice without fusion of the crystal. Solute molecules such as *n*-heptane and *n*-butylcyclohexane which would interfere with the rotation cannot be incorporated into the crystal lattice of 1,1-dimethylcyclohexane, hence, solid solution formation does not occur, and normal cryoscopic behavior is observed. The fact that abnormal behavior occurs when 2,2,3-trimethylbutane is used as the solute confirms the idea that it is the over-all size and shape of the molecule rather than its molecular species which determines whether or not a solid solution will result.

Experimental

Hydrocarbons.—The 1,1-dimethylcyclohexane and the hydrocarbons used as "impurities" were materials taken from the stock of the American Petroleum Institute Research Project 45 and were of good purity (99.0 mole % ± 0.5). When practicable, the 1,1-dimethylcyclohexane was separated from the "impurity" by fractional distillation at about 25-plate efficiency and re-used (after its freezing point had been checked) in the next determination, otherwise fresh solvent was used.

Apparatus.—The apparatus used in determining freezing points was essentially that described by Glasgow, Streiff and Rossini.[7] Temperatures were measured by means of a platinum resistance thermometer in connection with a Mueller resistance bridge (Leeds and Northrup, Type G-2). This thermometer was calibrated at the National Bureau of Standards.

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(7) Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

DEPARTMENT OF CHEMISTRY
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The Reaction of Diazonium Salts with Some 2-Thiouracils

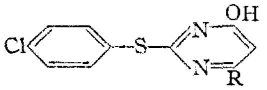
BY ELVIRA A. FALCO, GEORGE H. HITCHINGS AND PETER B. RUSSELL

Lythgoe, Todd and Topham[1] showed that pyrimidines suitably substituted in the 2,4-, 4,6- or 2,4,6-positions would undergo coupling with diazotized anilines in sodium carbonate or bicarbonate solution giving 5-phenylazo derivatives. They also investigated the structural conditions governing the coupling of pyrimidine derivatives. For this last purpose the dyes were not isolated, color being taken as an indication of coupling. They reported that 2-thiol-4,6-dihydroxy-, 2-thiol-4,6-diamino- and 2-thiol-4-hydroxy-6-methyl-pyrimidine underwent coupling.

In a recent paper Polonovski and Pesson[2] re-examined the reaction and arrived at the same general conclusions as the English authors regarding the nature of the products and the structural limitations of the reaction. They were, however, unable to couple 2-thiol-4-hydroxy-6-methylpyrimidine with diazonium salts, although they synthesized the brownish red 2-thiol-4-hydroxy-5-phenylazo-6-methylpyrimidine by condensation of thiourea with ethyl phenylazoacetoacetate.

Some time ago we examined the reactions of 2-thiol-4-hydroxypyrimidine and 2-thiol-4-hydroxy-6-methylpyrimidine with diazotized *p*-chloroaniline. When either of these compounds was allowed to react with the diazonium salt in carbonate or bicarbonate solution the following sequence of changes occurred. The solution turned pinkish red, solid separated and nitrogen was evolved. Examination of the solids revealed that they were not the expected 5-phenylazo compounds since on recrystallization from alcohol they were obtained colorless.

The product from 2-thiol-4-hydroxypyrimidine analyzed for $C_{10}H_7ON_2SCl$, while that from 2-thiol-4-hydroxy-6-methylpyrimidine gave analytical figures which agreed with the formula $C_{11}H_9ON_2SCl$. On heating with concentrated hydrochloric acid at 100° these compounds gave *p*-chlorothiophenol and uracil or 6-methyluracil, respectively. We concluded therefore that they were 2-(*p*-chlorophenylthio)-4-hydroxypyrimidine (I) and 2-(*p*-chlorophenylthio)-4-hydroxy-6-methylpyrimidine (II).



I, R = H
II, R = CH_3

The formation of *p*-chlorophenyl ethers of 2-thiolpyrimidines by this method is analogous to the formation of unsymmetrical diaryl and alkyl-aryl sulfides by the reaction of diazonium salts with the sodium salts of thiophenols or mercaptans.[3] In this instance the reaction proceeds *via* the diazosulfide (III) (R = alkyl or aryl). We did not isolate any product corresponding to III from the reaction of 2-thiolpyrimidines with

$$ArN_2^+X^- + RSNa \longrightarrow \underset{III}{ArN{=}NSR} \longrightarrow ArSR + N_2$$

diazonium salts. The fact that nitrogen is evolved in the cold would indicate that the 2-diazosulfides of pyrimidines are less stable than their aryl or alkyl analogs.

Unfortunately Polonovski's paper, no doubt unintentionally, gives the impression that previous students of the coupling reaction have been content to observe the appearance or non-appearance of a color reaction. In fact, Todd[1] demon-

(1) Lythgoe, Todd and Topham, *J. Chem. Soc.*, 315 (1944).

(2) Polonovski and Pesson, *Bull. soc. chim.*, [5] **15**, 688 (1948).

(3) Stadler, *Ber.*, **17**, 2675 (1884); Ziegler, *Ber.*, **23**, 2469 (1890).