carbon gave 23.5 g. (32.5%) of a yellow crystalline solid melting at 161–165°.

(b) **Thiourea.**—A solution of 15.2 g. (0.2 mole) of thiourea and 12.9 g. (0.1 mole) of I in water (200 ml.)-ethanol (50 ml.) and 42 ml. (0.5 mole) of concd. hydrochloric acid was heated at reflux (86°) for 10 hours. The solid crystalline precipitate that formed was recovered by filtration to give 9.3 g. (64.1%) of crude product melting at 158–162°. After two recrystallizations from ethanol–water (1–8) the light yellow solid melted at 161.5–164.5°. *Anal.* Calcd. for $C_6H_7NS_2$: C, 41.35; H, 4.86; N, 9.65; S, 44.15. Found: C, 41.52; H, 4.75; N, 9.64; S, 44.15.

(c) **Ammonium Dithiocarbamate.**—A 20% aqueous solution of ammonium dithiocarbamate (24 g., 0.25 mole) was added dropwise to a vigorously stirred suspension of I (25.8 g., 0.2 mole), hydrochloric acid (18.2 ml., 0.22 mole) and water (100 ml.). The temperature was maintained at 8–10° during the 1 hour period of addition. The light yellow, somewhat sticky solid which precipitated was recovered by filtration; repeated washing with hexane removed most of the impurities to give 16 g. (55%) of a white, crystalline compound melting at 157–160°. After further purification by extracting with benzene, the product melted at 160–162°.

2-Hydroxy-4,5-dimethylthiazole.—A mixture of 12.9 g. (0.1 mole) of I in water (150 ml.) and concd. hydrochloric acid (3.5 ml.) was heated at reflux (98°) for 11.5 hours. The white crystalline solid that formed when the solution was cooled was recovered by filtration. The solid (8 g.) melted at 140–146°. A further crop (1.2 g.) of slightly yellow crystals was obtained by concentrating the filtrate; yield 71.3%. Two recrystallizations from benzene gave large white crystals melting at 143–145°. *Anal.* Calcd. for C_5H_7NOS: C, 46.49; H, 5.46; N, 10.84; O, 12.39; S, 24.82. Found: C, 46.51; H, 5.46; N, 10.86; S, 24.87.

2-Chloro-4,5-dimethylthiazole.—Hydrogen chloride (95 g., 2.6 moles) was added to I (129 g., 1 mole) over a period of 1 hour at 20–30° while stirring the mixture. The resulting slurry was dissolved in 350 ml. of water, the water solution extracted three times with ether (100 ml. per extraction), and the ether solution was concentrated to give 96 g. of crude product. Hexane (100 ml.) was added to the crude product to precipitate 2-hydroxy-4,5-dimethylthiazole which had formed as a second product. There was obtained on distillation 74 g. (50%) of a colorless oil boiling at 49–53° (3 mm.), n^{20}_{D} 1.5307, d^{20}_{4} 1.233; $[MR]^{20}_{D}$ 36.92 (calcd.), 37.02 (found).

Anal. Calcd. for C_5H_6ClNS: C, 40.68; H, 4.07; Cl, 24.03; N, 9.49; S, 21.73. Found: C, 40.98; H, 4.09; Cl, 23.73; N, 9.37; S, 21.71.

2-Amino-4,5-dimethylthiazole Hydrochloride.—A solution of 107 g. (2.0 moles) of ammonium chloride and 32.25 g. (0.25 mole) of I in water (200 ml.)-ethanol (100 ml.) was heated at reflux (85°) for 5.5 hours. The white crystalline product that formed on cooling was isolated by filtration. After single washes with ice-cold water and acetone the product on drying weighed 41 g. (100%), m.p. 250° (dec.). Further washing with ice-cold water (twice) and acetone (once) gave 26.1 g. (63.5%) of white crystals melting at 262–263° (dec.). *Anal.* Calcd. for $C_5H_9ClN_2S$: C, 36.47; H, 5.51; Cl, 21.54; N, 17.01; S, 19.47. Found: C, 36.50; H, 5.49; Cl, 21.59; N, 17.10; S, 19.49.

Acknowledgment.—The analyses of all compounds were made by James R. Kubik, Arthur K. Kuder and Huffman Microanalytical Laboratories. Sincere appreciation is expressed to James A. Early, Martin Smilek and Paul Rohrer for their assistance with some of the experimental work reported here.

BRECKSVILLE, OHIO RECEIVED OCTOBER 1, 1951

[CONTRIBUTION FROM THE WHITMORE LABORATORY, PENNSYLVANIA STATE COLLEGE]

Urea and Thiourea Adduction of C_5–C_{42}-Hydrocarbons

BY ROBERT W. SCHIESSLER AND DAVID FLITTER

Unbranched *n*-paraffins above hexane readily form crystalline complexes with urea at 25°. If the *n*-alkyl chain is sufficiently long, terminal cyclization does not prevent urea adduction, whereas a methyl group centered on a C_{13}-chain inhibits crystalline complex formation. Hydrocarbons widely differing in structure will form crystalline complexes with thiourea at room temperature if the cross-sectional dimensions of the molecule are 5.8 ± 0.5 Å. by 6.8 ± 0.3 Å. as estimated from measurement of the Fisher–Hirschfelder models. Thiourea adduct does not form readily if the molecular dimensions are near the tolerance limits, and such an adduct will be unstable. Phenyl groups appear to interfere with the formation of urea and thiourea complexes. Normal paraffin chains, attached to otherwise suitable structures, interfere with thiourea adduction.

The formation of crystalline complexes between certain hydrocarbons and urea[1,2] or thiourea[3] has been the subject of several recent investigations.[4-11] Since better definition of the hydrocarbon structural requirements for adduct formation is important to the understanding and utility of the processes, and since a great variety of hydrocarbons covering the C_5–C_{42} range is available in this Laboratory from the work of the American Petroleum Institute Research Project 42,[12] we have investigated the tendency of the latter to form adducts at 25° with the two reagents. Certain regularities have been noted, and, in the case of thiourea, empirical treatment based on measurements of Fisher–Hirschfelder models[13] has led to a new correlation of structure and adductibility.

A standardized test procedure was employed which differed slightly for the urea and thiourea experiments.

Experimental

1. **Reagents.**—Urea, C.P. Coleman and Bell, Norwood, Ohio. Thiourea, C.P. Coleman and Bell, Norwood, Ohio. Methanol, commercial synthetic, fractionally distilled in a glass helix-packed column of 40 plates, n^{20}_{D} 1.3296. Hydrocarbons, from A.P.I. Research Project 42, this Laboratory. Benzene, anhydrous commercial, to which was added half the amount of water needed for saturation at room temperature. Methyl ethyl ketone, Shell Chemical, technical.

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(1) F. Bengen, German Patent Application, O.Z. 12438, 1940.

(2) F. Bengen and W. Schlenk, *Experientia*, **5**, 200 (1949).

(3) B. Angla, *Compt. rend.*, **224**, 402 (1947).

(4) L. C. Fetterly, U. S. Patent 2,499,820, 1947.

(5) B. Angla, *Ann. chim.*, [12] **4**, 677 (1949).

(6) W. J. Zimmerschied, *et al.*, THIS JOURNAL, **71**, 2947 (1949).

(7) W. J. Zimmerschied, *et al.*, *Ind. Eng. Chem.*, **42**, 1300 (1950).

(8) W. Schlenk, *Ann.*, **565**, 204 (1949); *Experientia*, **6**, 292 (1950); *Fortschritte Chem. Forschung*, **2**, 92 (1951).

(9) O. Redlich, *et al.*, THIS JOURNAL, **72**, 4153 (1950).

(10) O. Redlich, *et al.*, *ibid.*, **72**, 4161 (1950).

(11) A. E. Smith, *J. Chem. Phys.*, **18**, 150 (1950).

(12) Advisory Committee: H. Sutherland (Chairman), E. M. Barber, J. R. Bates, L. C. Beard, Jr., G. H. Denison, L. M. Henderson, R. G. Larsen, R. F. Marschner, J. H. Ramser. Presented before the XIIth International Congress on Pure and Applied Chemistry, New York, N. Y., September, 1951.

(13) Fisher Scientific Company, Pittsburgh, Pa.

2. **Procedure.**—Saturated solutions of urea or thiourea in methanol were prepared by adding an excess of the reagent and equilibrating at room temperature. In the case of the urea tests, *ca.* 0.5 cc. of hydrocarbon was placed in a 10-cc. ampoule, 5–6 cc. of saturated urea solution added and the ampoule sealed. If the hydrocarbon was a solid, it was warmed with several drops of benzene to effect solution before the urea–methanol was added. The ampoules were then machine-shaken at room temperature for two weeks, observing the sample for changes at various time intervals.

The thiourea tests were carried out similarly, but the samples were contained in 10-cc. corked vials and were not shaken by machine. It was found that the addition of several drops of 1/1 methyl ethyl ketone/benzene solution caused adduct to form more quickly. The methanol solutions were added slowly since the bulky adduct initially formed in some instances dissolved on addition of more of the reagent. The precipitates were collected on a small sintered glass filter and dried by suction. Washing was a matter of judgment since many of the complexes are so unstable as to be decomposed by the washing solvent.[14] Wherever possible, the urea precipitates were washed with one cc. of 2,2',4-trimethylpentane, then with one cc. of pentane. The thiourea precipitates were washed with pentane only. Whenever addition of these solvents caused the bulky appearance of the precipitate to change, the washing was immediately stopped.

3. **Detection of Crystalline Complex.**—Adduct formation, observed as voluminous precipitate, was confirmed on the air-dried solid materials by one or more of the following methods: (a) Decomposition with hot water caused the hydrocarbon to separate as an oily layer. (b) Examination under 50-power magnification. Both the urea and thiourea adducts appear as long, thin needles, very different from the pure reagents. Regardless of the hydrocarbon adducted, the crystals appeared similar. (c) Capillary melting point. This test is not very definitive for urea adducts since adducts and hydrocarbon–urea mixtures behaved alike, and pure urea melted only slightly more sharply. For thiourea, the presence of hydrocarbon, either adducted or physically admixed, always produced a translucent melt very different from pure thiourea.

Results

Thirty-two pure hydrocarbons were tested with urea and fifty with thiourea. The results are summarized in Tables I and II. The notation C_x refers to a saturated straight carbon chain of x carbon atoms.

TABLE I

Adducting with Urea at 25°

- *n*-Heptane
- *n*-Tridecane
- 1-Tridecene
- *n*-Tetradecane
- *n*-Hexacosane
- *n*-Octacosane
- *n*-Hexatriacontane
- 1-Phenyleicosane
- 1-Cyclohexyleicosane
- 1-Cyclopentylheneicosane

Non-Adducting with Urea at 25°

- *n*-Pentane
- *n*-Hexane
- 2,2,4-Trimethylpentane
- 7-Methyltridecane
- 3-Ethyltetracosane
- 5-*n*-Butyldocosane
- 9-*n*-Butyldocosane
- 11-*n*-Butyldocosane
- 7-*n*-Hexyldocosane
- 3-Ethyl-5-(2-ethylbutyl)-octadecane
- 1-Phenyloctane
- 2-Phenyleicosane
- 17-Phenyltriacontane
- 1-Cyclohexyloctane
- 2-Cyclohexyleicosane
- 9-Cyclohexyleicosane
- 1,4-Di-*n*-decylcyclohexane
- 1-α-Naphthylpentadecane
- 1-α-Decalylpentadecane
- 1-α-*n*-Hexadecylhydrindene
- 1-α-*n*-Hexadecylhydrindane
- 1-Cyclopentyl-2-hexadecylcyclopentane

TABLE II

Adducting with Thiourea at 25°

- Neopentane
- 2,2,4-Trimethylpentane
- 3-Ethyltetracosane
- Cyclopentane
- Cyclopentene
- Ethylcyclopentane
- 1,1-Dimethylcyclopentane
- 1,1,2-Trimethylcyclopentane
- 1-Methyl-1-ethylcyclopentane
- *cis*-1-Methyl-3-ethylcyclopentane
- *trans*-1-Methyl-3-ethylcyclopentane
- Cyclohexane
- Methylcyclohexane
- 1-Cyclohexyloctane
- 1-Cyclohexyleicosane
- 1,4-Di-*n*-decylcyclohexane
- *exo*-Perhydro-4,7-methanoindene
- 2-Cyclohexyleicosane
- 1,2-Dicyclohexylethane
- 1-Cyclohexyl-3-cyclopentylpropane
- 1-Phenyl-2-cyclohexylethane
- 1-Cyclopentylheneicosane
- Dicyclopentyl
- *cis*-(0,3,3)-Bicyclooctane
- 1,3-Dicyclopentylcyclopentane

Non-adducting with Thiourea at 25°

- 5-*n*-Butylnonane
- 5-*n*-Butyl-4-nonene
- 3-Methylheptane
- 2,2,3,3,5,6,6-Heptamethylheptane
- 2,2,3,5,5,6,6-Heptamethyl-3-heptene
- 1,1-Dicyclohexyltetradecane
- 1-Cyclopentyl-2-hexadecylcyclopentane
- 1-Phenyloctane
- 1-Phenyleicosane
- 2-Phenyleicosane
- 1,2-Di-α-naphthylethane
- Tricyclohexylmethane
- 1,1-Dicyclohexylethane
- 9-Cyclohexyleicosane
- 1,2-Diphenylethane
- 1,4-Diphenylbutane
- α-*n*-Hexadecylhydrindane
- 9-*n*-Butylperhydroanthracene
- 9-*n*-Dodecylperhydroanthracene
- 9-*n*-Dodecylperhydrophenanthrene
- 2,2,4,15,17,17-Hexamethyl-7,12-di-(3,5,5-trimethylhexyl)-octadecane
- 1,2,3,4,5,6,7,8,9,10,17,18-Dodecahydro-9-(*n*-octyl)-naphthacene

Discussion

1. **Urea Adducts.**—As reported by other investigators, these results show that the principal requirement for hydrocarbon adduction with urea is a long, unbranched chain. A methyl group at the middle of an *n*-C_{13} chain prevents adduction. Neither terminal olefinic double bond nor a terminal monocyclic group on a long chain prevents adduction, and an interesting pair in this connection is 3-ethyltetracosane and 1-cyclopentylheneicosane. Both have an entity of five carbon atoms attached to a straight chain of twenty-one carbon atoms. While the rigid cyclic arrangement of five does not interfere, the freely rotating ethyl groups in 3-ethyltetracosane prevent urea adduction. X-Ray studies by Smith[11] have indicated the general structural requirements for stable urea–hydrocarbon complexes.

2. **Thiourea Adducts.**—The structural requirements in this case have not been indicated by previous workers. Because of the variety of hydrocarbon types which adduct the picture is more complex than with urea. Mere branching is insufficient and there appears to be some kind of specificity connected with thiourea adduction. Aside from Smith's statement that the larger radius of the sulfur atom results in a larger channel in the thiourea spiral, thus accommodating certain hydrocarbons, and Redlich's observation that no simple relationship appears to exist between hydrocarbon structure and stability of thiourea complex, the literature offers nothing toward the solution of this problem.

In an attempt to find the elusive basis for thiourea adduction, measurements were made in this Laboratory on molecular models of a number of key hydrocarbon structures. The models were the Fisher–Hirschfelder–Taylor type. The rotational

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[14] Quantitative composition data on the adducts were unobtainable for the following reasons: (a) Purification of the adducts requires washing with both hydrocarbon and urea solvents, both of which decompose the complexes. For accurate analysis, a macroscopic quantity of adduct is needed in order to adequately overcome this difficulty. (b) The rarity of the hydrocarbons studied precluded the preparation of macroscopic amounts of the adducts.

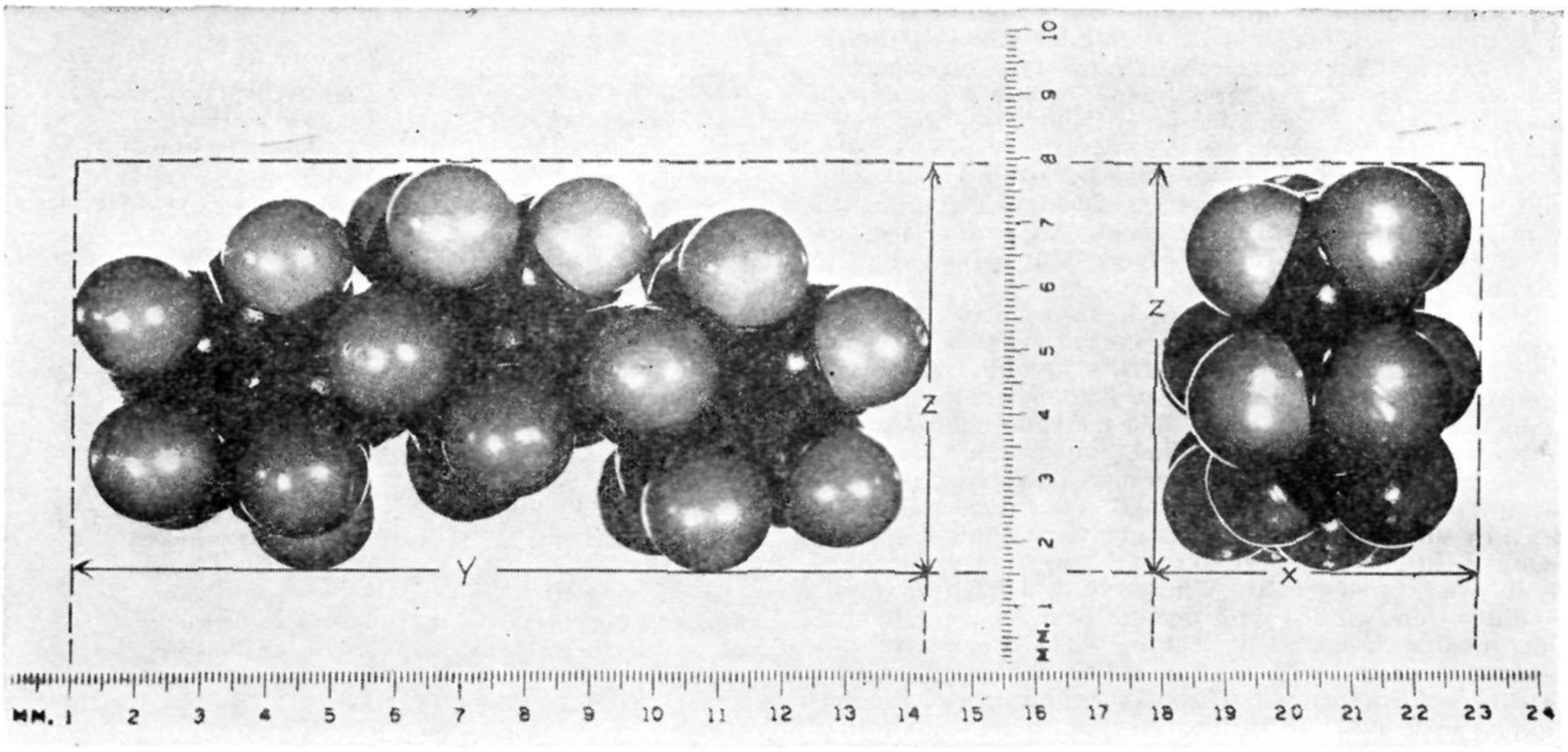


Fig. 1.—Dimensional views of *trans*-1,3-dicyclopentylcyclopentane, showing method of measurement: x = 5.3 cm., z = 6.5 cm. Forms adduct with thiourea.

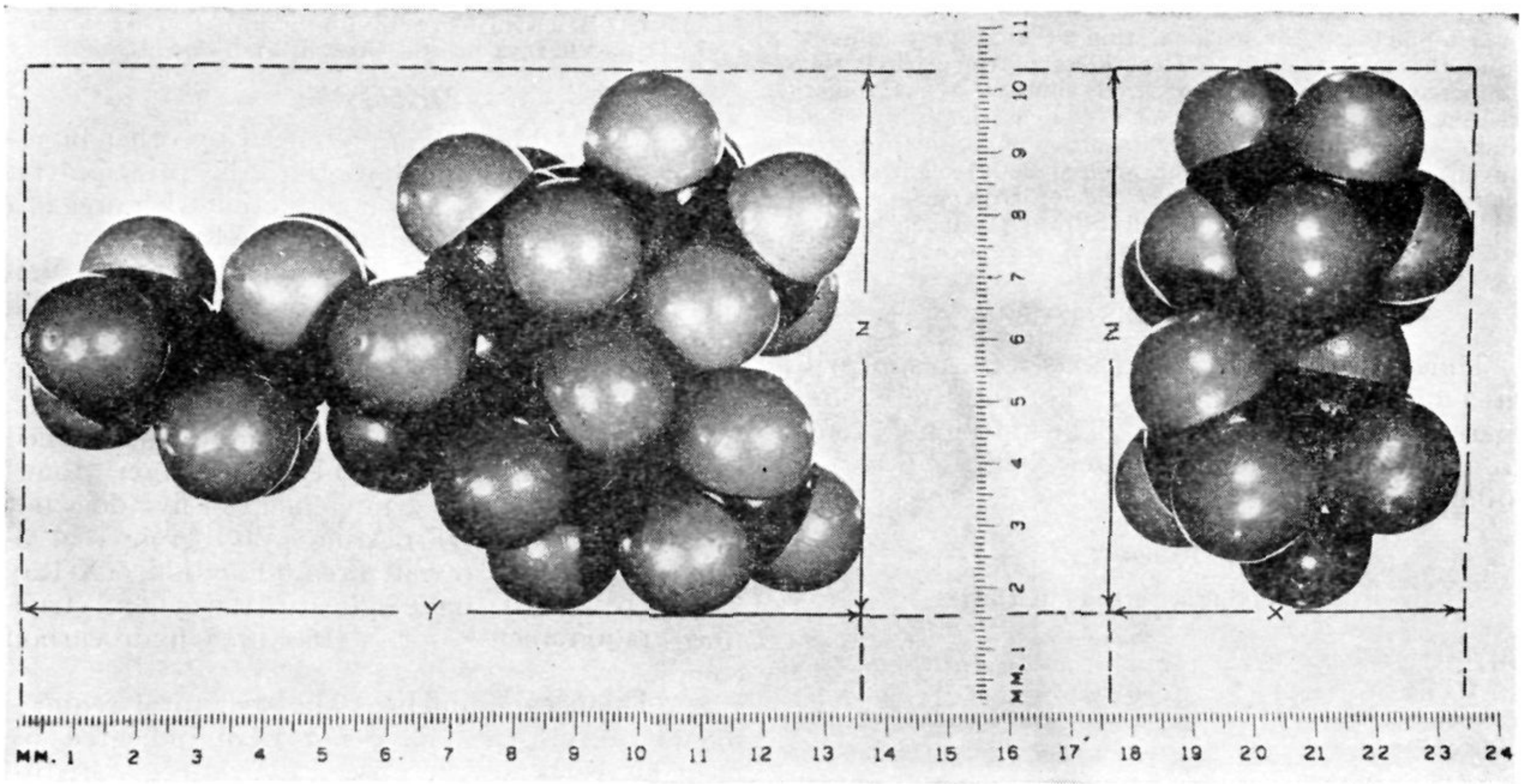


Fig. 2.—Dimensional views of 5-*n*-butylnonane, showing axes measured: x = 5.8 cm., z = 8.9 cm. Does not form adduct with thiourea.

isomer forms chosen for measurement were those most closely approaching a fit into a cross section of 6.5 × 6.5 cm., measurements being then made along the x, y and z axes. For some hydrocarbons several forms were measured, since in the liquid state the various possible structures may be viewed as being in dynamic equilibrium so that the entire mass may shift over to the required form as adduct is produced. As a first approximation the median cross section of adducting hydrocarbons was determined. Using this as a criterion, only that form was retained for averaging which was closest to the median. If several forms seemed to have equal value they were also retained. Thus the average cross section dimensions were determined and found to be 5.8 × 6.8 cm. The maximum deviations are ±0.8 and ±0.6, respectively, while the average deviations are 0.5 and 0.3, respectively, without regard to sign.

Figures 1 and 2 illustrate the method used, and the measurements are summarized in Tables III and IV, showing the ratio of the axial lengths to 5.8 or 6.8 cm.

The average cross section of the non-adductors is 6.2 × 9.4 cm. The maximum deviations are ±1.2 and ±2.6, respectively, while the respective aver-

TABLE III

MEASUREMENTS OF THIOUREA-ADDUCTING HYDROCARBONS

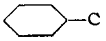
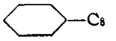
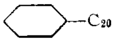
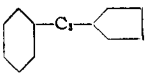
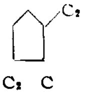
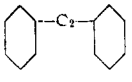
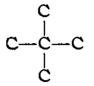
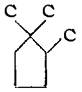
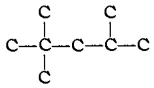
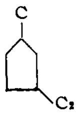
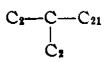
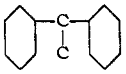
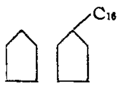
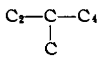
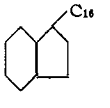
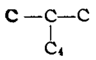
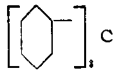
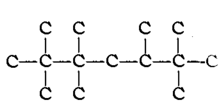
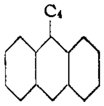
Hydrocarbon	$x/5.8$	$z/6.8$	Hydrocarbon	$x/5.8$	$z/6.8$
	0.90	1.01		0.95	0.94
	.90	1.01		0.91	0.96
	.90	1.01		1.02	.91
	.90	1.01		1.12	1.04
	1.10	0.94		0.92	1.07
	0.86	.94		.92	1.07
	1.09	.97	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$	1.07	0.94
	1.12	1.06	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}\overset{C}{C}{-}C}$	1.02	.96
 *trans* *cis*	1.09 1.10	0.94 .99	 $\mathrm{C_2{-}\underset{C_2}{C}{-}C_{21}}$	0.90	1.07

TABLE IV

MEASUREMENTS OF THIOUREA NON-ADDUCTING HYDROCARBONS

Hydrocarbon	$x/5.8$	$z/6.8$	Hydrocarbon	$x/5.8$	$z/6.8$
	0.98	1.21		1.02	1.35
 $\mathrm{C_2{-}\underset{C}{C}{-}C_4}$	0.88	1.00		1.26	1.15
 $\mathrm{C{-}\underset{C_4}{C}{-}C}$	1.00	1.31		1.26	1.75
 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}C{-}\overset{C}{C}{-}\overset{C}{\underset{C}{C}}{-}C}$	1.17	1.07		1.05	1.68

age deviations are 0.7 and 1.6 without regard to sign.

An important class of non-adducting hydrocarbons is that in which an aromatic ring is present. Although the dimensions are very close to those of the corresponding cyclohexyl structures, no adduction occurs. Angla[5] reported similar results with olefinic structures and concluded that the electron-releasing double bond had an unfavorable effect on thiourea adduction since the reagent itself was quite anionoid. 1-Phenyl-2-cyclohexylethane adducts probably because of the preponderating effect of the rest of the molecule.

Redlich[10] has described results on an interesting pair of hydrocarbons, 2,2- and 2,3-dimethylbutane, finding that adduct of the 2,2-isomer was considerably more stable. Measurements of the models show that both isomers should adduct with thiourea. However, the 2,2-isomer can exist in only one form, this having cross sectional axes of 6.0 × 6.4 cm. whereas the 2,3-isomer can exist in three forms, the *cis* and intermediate forms having suitable cross sections. Possibly the relative instability of the 2,3-isomer adduct is due to the fact that it contains hydrocarbon in the less stable form at room temperature.

From this work, it appears that where opposing structural factors are present the predominant one will reveal itself by the behavior of the hydrocarbon toward thiourea. The example of 1-phenyl-2-cyclohexylethane has already been mentioned. Cyclopentane, cyclohexane and 2,2,4-trimethylpentane adduct with ease while 1-cyclopentylheneicosane, 1-cyclohexyleicosane and 3-ethyltetracosane form thiourea adducts with difficulty. Apparently the long normal alkyl chains in the latter hydrocarbons, which are of the type unsuitable for thiourea adduction, greatly reduce the stability of the complex.

The model measurements correlate well with published data bearing on this problem. X-Ray data[15,16] show the diameter of a normal paraffin chain to be 3.8–4.2 Å. The dimensions of the channel in the urea adduct of *n*-hexadecane are 4.1 × 4.8 Å., as calculated from Smith's data,[11] in good agreement with 4.0 × 4.6 Å., obtained from our measurement of the Fisher–Hirschfelder model of a normal paraffin chain.[17]

On the basis of these correlations and the measurements given, it is reasonable to predict that the channel in thiourea adducts will have dimensions approximating 5.8 × 6.8 Å.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

STATE COLLEGE, PENNA. RECEIVED JULY 31, 1951

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[15] A. Müller, *Proc. Roy. Soc.* (*London*), **120**, 437 (1928).

[16] Private communication, L. C. Roess, Beacon Laboratories, Texas Co., Beacon, N. Y.

[17] Fisher–Hirschfelder models are scaled 1 cm. per 1 Å.