side is not strictly simple. This trend away from simple dispersion is even more evident in *p*-phenylazophenyl tetraacetyl-β-D-galactoside, where the discrepancies in rotation between those observed and those calculated by equation (1) are even greater. It is interesting to note in Table I that the negative rotation of the unacylated glycosides become more negative with decreasing wave length, whereas the positive rotation of the acetylated galactoside becomes more positive. No attempts were made to extend dispersion measurements to other *p*-phenylazophenyl β-D-glycosides because of the comparatively low specific rotations of the known members of this class[5] and the high extinction coefficients of their absorption bands.[3]

Experimental Part

Dispersion measurements were made with a Lippich–Landolt precision polarimeter no. 80 and spectroscope monochromator no. 85[6] manufactured and calibrated by O. C. Rudolph and Sons. Solutions of the *p*-phenylazophenyl β-D-glycoside (10^{-1} molar for the glucoside and galactoside and 5×10^{-2} molar for the acetylated galactoside) were made in commercial dioxane and placed in a 10-ml. 1-dcm. polarimeter tube. Measurements were made at room temperature (*ca.* 23°) with no thermostating. Readings were taken at wave lengths indicated in Table I. The half-shade angle of the polarimeter was kept at 5 on its scale during all readings, and the slit widths on the monochromator were varied between 0.3 and 0.6 mm. depending upon the amount of light which would traverse the solution. Measurements were made at the concentrations indicated until increasing optical densities with decreasing wave length made matching of the polarimeter field impossible. At this point the solutions were diluted to 50% of their initial concentration with dioxane. Readings were continued until dilution was again necessary. One or two dilutions were usually sufficient to obtain data as in Table I. The dilution technique could not be employed to permit lower wave length readings as the observed rotation rapidly decreased with each dilution until the experimental errors of measurement made the results meaningless for comparative purposes.

Summary

Rotatory dispersion measurements on *p*-phenylazophenyl β-D-glucoside, β-D-galactoside, and tetraacetyl-β-D-galactoside have been conducted in order to see if the isolated azo chromophore of the aglycone might cause anomalous dispersion by interacting with the asymmetric centers through the conjugation of the benzene ring. The high extinction coefficients characteristic of the absorption bands in the aglycone, however, prevented dispersion measurements as the wave length of the first absorption band was approached.

In the transparent regions of the spectrum the dispersion of the unacylated glycosides was very nearly simple. Divergencies from simple behavior of possible significance were observed as the first absorption band of the aglycone was approached.

The wave length of the active absorption band calculated from a simple Drude equation agreed very well with the wave length of the ultraviolet absorption band as measured spectrophotometrically, indicating that the isolated azo chromophore in the aglycone had no effect on the rotation in the visible regions of the spectrum.

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[6] Purchased with a grant kindly furnished by The Research Corporation, New York.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXV. Some Heat Capacity, Entropy and Free Energy Data for Nine Hydrocarbons of High Molecular Weight

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In a series of investigations carried out at Stanford University between 1937 and 1944 heat capacity measurements were made upon twelve hydrocarbons of high molecular weight. From the data thus obtained the corresponding molal entropies were derived and in most instances the free energies of formation were also computed with the aid of available heats of combustion. Results for three of these hydrocarbons (11-*n*-decylheneicosane,[1] and *cis*- and *trans*-decahydronaphthalene[2]) have already been published in other connections. In the present paper we shall present similar results for the remaining nine compounds: *n*-hexadecane, *n*-octadecane, *n*-tetracosane, *n*-dotriacontane, ethylcyclohexane, *n*-heptylcyclohexane, *n*-dodecylcyclohexane, 11-cyclohexylheneicosane and 11-phenylheneicosane.

Materials

The hydrocarbon samples were the best obtainable at the time of these measurements, although more recently *n*-hexadecane and ethylcyclohexane have become available in much purer form. Most of the materials were also used in This Laboratory in determinations of the heats of combustion, in which work non-hydrocarbon impurities are especially serious. Accordingly, appropriate tests were run for ash content, the presence of halogens and in

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[1] F. B. Fischl, B. F. Naylor, C. W. Ziemer, G. S. Parks and J. G. Aston, THIS JOURNAL, **67**, 2075 (1945).

[2] G. S. Parks and J. A. Hatton, *ibid.*, **71**, 2773 (1949).

some cases the carbon-hydrogen ratio. The results of such tests were entirely satisfactory for the materials used in this study. The observed melting points and the mole % purity, as estimated in the course of fusion determinations, are given in Table I. In all cases the impurities in the samples must have been primarily isomers or neighboring members of a homologous series, and these should not produce appreciable errors in the measured heat capacities except in the temperature region approaching the melting point.

TABLE I

MELTING POINTS AND ESTIMATED PURITY

Hydrocarbon	Formula	M. p., °K.	Purity, mole %
n-Hexadecane	$C_{16}H_{34}$	290.2	95.
n-Octadecane	$C_{18}H_{38}$	300.8	96.0
n-Tetracosane	$C_{24}H_{50}$	323.0	..
n-Dotriacontane	$C_{32}H_{66}$	342.7	..
Ethylcyclohexane	C_8H_{16}	161.2	99.1
n-Heptylcyclohexane	$C_{13}H_{26}$	232.0	97.1
n-Dodecylcyclohexane	$C_{18}H_{36}$	285.6	98.8
11-Cyclohexylheneicosane	$C_{27}H_{54}$	266.5	96.7
11-Phenylheneicosane	$C_{27}H_{48}$	294.0	97.7

The sources of our samples of *n*-hexadecane and *n*-octadecane were Eastman Kodak Co. materials, which were further purified in the procedures described, respectively, by Richardson and Parks[3] and by Parks[4] and coworkers. On the other hand, the Eastman *n*-tetracosane and *n*-dotriacontane were used without any additional purification. The ethylcyclohexane was part of a preparation from the laboratory of Professor C. E. Boord of Ohio State University. The samples of *n*-heptylcyclohexane and *n*-dodecylcyclohexane were prepared at Stanford University under the direction of Professor C. R. Noller, and their properties have been described in detail by Moore, Renquist and Parks.[5] The 11-cyclohexylheneicosane and 11-phenylheneicosane were compounds prepared in the work of American Petroleum Institute Research Project 42 at the Pennsylvania State College.[6]

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[7] In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is ordinarily less than 0.7%, except insofar as impurities in a sample may cause premelting at the upper temperatures of the crystals. The fortuitous errors are usually under 0.25%; and this latter figure may also be considered our probable *relative* error in making comparisons among these hydrocarbons.

Generally more than forty specific heat determinations in the temperature interval between 78 and 300°K. were made on each hydrocarbon. The results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read off from this curve for various even temperatures. For the sake of spatial economy and ease of comparison these derived values, rather than the more numerous experimental ones, are recorded in Table II. They and also the fusion data of Table III are expressed in terms of the *defined* conventional calorie[8] and with all weights reduced to a vacuum basis.

Three of these hydrocarbons exhibited small but distinct "humps" in the specific heat curves for the crystals. In the case of *n*-octadecane this hump came within the interval 228–240°K. and yielded a locally maximum C_p value of 0.365 cal. per gram at 237°. For *n*-tetradecane the hump range was 250–265° with a maximum of 0.420 cal. per gram for C_p at 262°, and for *n*-dodecylcyclohexane the range was 229–249° with a maximum of about 0.380 at 245°K.

Several of these liquid hydrocarbons could be supercooled to some extent, and in particular the ethylcyclohexane was first obtained as a typical glassy material at the temperature of liquid air. In this state it showed C_p values per gram of 0.175, 0.330 and 0.328 at 97, 100 and 110°K., respectively.

Apparently the recent investigation of the heat capacities of ethylcyclohexane by Huffman, Todd and Oliver[9] provides us with the only comparable data now available for any of these compounds. These investigators worked with a purer material than ours, and obtained specific heats which, outside of our premelting range, average 0.35% lower than our curve and a heat of fusion which is 0.68% above our mean value.

Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.16°K. for these nine hydrocarbons. The detailed data are given in Table IV. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffmann[10] for estimating the entropy increases of the crystals from 0 to 80°K. The various increments from 80 to 298.16°K., which appear in the next three columns, were obtained by the usual methods directly from the experimental data. The results for the total entropy are then given in the second column from the right under the designation "S^0_{298}"; they are probably reliable to within 1% in an absolute sense and to about half this figure for comparative purposes. In this connection it should be noted that the later and more ac-

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[3] J. W. Richardson and G. S. Parks, THIS JOURNAL, **61**, 3543 (1939).

[4] G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, *ibid.*, **68**, 2524 (1946).

[5] G. E. Moore, M. L. Renquist and G. S. Parks, *ibid.*, **62**, 1505 (1940).

[6] F. C. Whitmore, J. N. Cosby, W. S. Sloatman and D. G. Clarke, *ibid.*, **64**, 1801 (1942).

[7] G. S. Parks, *ibid.*, **47**, 338 (1925); also G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[8] The factor 1/4.1833 has been used in converting the international joule to the defined calorie.

[9] H. M. Huffman, S. S. Todd and G. D. Oliver, THIS JOURNAL, **71**, 584 (1949).

[10] K. K. Kelley, G. A. Parks and H. M. Huffman, *J. Phys. Chem.*, **33**, 1802 (1929). In the case of compounds like 11-cyclohexylheneicosane, a weighted mean of the entropy extrapolations as calculated with the aliphatic and cyclic constants has been used.

TABLE II

SPECIFIC HEATS (C_p) IN CALORIES PER GRAM OF SUBSTANCE

s = crystalline; *l* = liquid

T, °K.	$C_{16}H_{34}$	$C_{18}H_{38}$	$C_{24}H_{50}$	$C_{32}H_{66}$	C_8H_{16}	$C_{13}H_{26}$	$C_{18}H_{36}$	$C_{27}H_{54}$	$C_{27}H_{48}$
80	0.1591 *s*	0.1552 *s*	0.1498 *s*	0.1477 *s*	0.1407 *s*	0.1432 *s*	0.1388 *s*	0.1411 *s*	0.1375 *s*
90	.1745	.1707	.1653	.1613	.1531	.1557	.1513	.1560	.1493
100	.1885	.1842	.1800	.1745	.1654	.1680	.1630	.1681	.1610
110	.2013	.1967	.1935	.1875	.1775	.1801	.1742	.1788	.1725
120	.2134	.2082	.2057	.2004	.1896	.1922	.1855	.1902	.1840
130	.2251	.2200	.2165	.2126	.2019	.2047	.1968	.2015	.1945
140	.2360	.2318	.2262	.2228	.216	.2180	.2072	.2125	.2040
150	.2464	.2426	.2359	.2320	.252 *s*	.2314	.2173	.2234	.2128
160	.2565	.2535	.2465	.2417	.3410 *l*	.2410	.2275	.2345	.2224
170	.2675	.2648	.2582	.2524	.3475	.2500	.2378	.2436	.2318
180	.2784	.2762	.2705	.2639	.3540	.2628	.2485	.2538	.2413
190	.2895	.2881	.2825	.2757	.3605	.279	.2598	.2657	.2510
200	.3010	.3011	.2947	.2885	.3676	.302 *s*	.2719	.2778	.2620
210	.3135	.3153	.3074	.3030	.3750	......	.2838	.2899	.2737
220	.3265	.3285	.3230	.3176	.3823	......	.2955	.3019	.2850
230	.341	.349	.3396	.3333	.3895	......	.3110	.3164	.2968
240	.359	.355	.358	.349	.3967	.4269 *l*	.338	.3340	.3090
250	.380	.365	.382	.367	.4050	.4344	.338	.358 *s*	.3210
260	.405	.381	.413	.386	.4150	.4421	.359	......	.334
270	.445 *s*	.404	.410	.405	.4250	.4505	.416 *s*	.471 *l*	.352
280	......	.456 *s*	.432	.426	.436	.460	......	.482	.388 *s*
290	.528 *l*	......	.474	.447	.447	.469	.488 *l*	.491	.....
300	.533 *l*	.530 *l*	.526 *s*	.469 *s*	.458 *l*	.478 *l*	.496 *l*	.498 *l*	.491 *l*

TABLE III

FUSION DATA[a]

Hydrocarbon	M. p., °K.	Heat of fusion (cal. per g.) I	II	Mean
n-Hexadecane	291.1	54.40	...	54.40
n-Octadecane	301.3	56.68	56.93	56.80
Ethylcyclohexane	161.4	17.64	17.61	17.63
n-Heptylcyclohexane	232.8	28.97	29.29	29.13
n-Dodecylcyclohexane	285.8	43.42	43.36	43.39
11-Cyclohexylheneicosane	266.9	30.82	30.63	30.73
11-Phenylheneicosane	294.3	41.56	41.52	41.54

[a] In the calculation of these fusion values, the somewhat more rapid rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

curate entropy result of Huffman[9] and co-workers for ethylcyclohexane is only about 0.23% less than our value tabulated here.

For the cases of *n*-octadecane and *n*-dotriacontane, which are crystalline substances at 298.16° K., we have also computed the entropy changes in the hypothetical fusion process at this temperature so as to be able to compare these compounds with others in the liquid state. In these computations we have used for the octadecane our own fusion data in Table III and for dotriacontane the estimate made by Parks and Rowe[11] for the heat of fusion.

The values of the entropies of formation (ΔS_f^0) given in the extreme right-hand column of Table IV represent simply the differences between the S_{298}^0 for each hydrocarbon and the corresponding values for the entropies contained therein. For this purpose we have used 31.211 e. u. for the entropy of hydrogen and 1.361 e. u. for C (β-graphite).[12]

While it is the intention of the senior author to present elsewhere in the near future a review of entropy regularities among both hydrocarbons and representative organic compounds containing oxygen, a few significant features relating to these tabulated S_{298}^0 values may be briefly noted here. Thus there is a fairly constant effect per CH_2 increment. Starting with the value of 70.76 e. u. as obtained by Douslin and Huffman[13] for liquid *n*-hexane, we find an average increase of 7.90 per CH_2 in going up the liquid paraffin series to *n*-hexadecane, 7.98 to *n*-octadecane and 8.05 e. u. to the hypothetical liquid *n*-dotriacontane. Likewise, there is an average increase of 7.98 e. u. per CH_2 increment in the liquid cyclohexane series from the ethyl to the dodecyl compound. By similar reasoning, the value of 51.3 e. u. may be assigned as the entropy contribution of the cyclohexyl group in a normal cyclohexane series involving liquids. On the other hand, the introduction of the cyclohexyl and phenyl groups in the middle of the heneicosane chain apparently produces entropy decreases, due to branching, of 7.6 and 5.4 e. u., respectively.

Free Energy Data

We have also calculated the free energies of formation of these hydrocarbons (except *n*-tetra-

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[11] G. S. Parks and R. D. Rowe, *J. Chem. Phys.*, **14**, 507 (1946).

[12] D. D. Wagman, J. E. Kirkpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[13] D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 1704 (1946).

TABLE IV

ENTROPIES OF THE HYDROCARBONS IN CALORIES PER DEGREE PER MOLE

s = crystalline; *l* = liquid

Substance	Molecular weight	Crystals 0–80°K.	Crystals Above 80°K.	Fusion	Liquid	S^0_{298}	$-\Delta S^0_f$ at 298.16°K.
n-Hexadecane (*l*)	226.432	27.88	76.82	42.31	2.83	149.8	402.56
n-Octadecane (*s*)	254.484	30.52	88.21			118.7	498.81
n-Octadecane (*l*)				47.77		166.5	451.01
n-Tetracosane (*s*)	338.640	38.36	117.23			155.6	657.34
n-Dotriacontane (*s*)	450.848	51.33	152.21			203.5	870.01
n-Dotriacontane (*l*)				76.5		280.0	793.51
Ethylcyclohexane (*l*)	112.208	13.80	14.55	12.25	26.66	67.3	193.28
n-Heptylcyclohexane (*l*)	182.338	21.52	42.28	22.82	20.17	106.8	316.63
n-Dodecylcyclohexane (*l*)	252.468	28.51	75.02	38.33	5.22	147.1	439.19
11-Cyclohexylheneicosane (*l*)	378.702	41.80	105.60	43.59	20.28	211.3	668.14
11-Phenylheneicosane (*l*)	372.654	41.12	111.36	52.60	2.37	207.4	578.41

cosane) by means of the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$. The results as well as the contributing enthalpy data are recorded in Table V, where for comparative purposes we have included a result for 11-*n*-decylheneicosane, based on the entropy value of Naylor and Parks.[1]

TABLE V

ENTHALPIES AND FREE ENERGIES AT 298.16°K.

In kcal. per mole

Substance	ΔH^0_f	ΔF^0_f
n-Hexadecane (*l*)	−108.72	11.30
n-Octadecane (*s*)	−135.92	12.80
n-Octadecane (*l*)	−121.54	12.94
n-Dotriacontane (*s*)	−231.82	27.58
n-Dotriacontane (*l*)	−205.36	31.23
Ethylcyclohexane (*l*)	−50.72	6.91
n-Heptylcyclohexane (*l*)	− 84.51	9.90
n-Dodecylcyclohexane (*l*)	−112.01	18.94
11-*n*-Decylheneicosane (*l*)	−201.72	30.38
11-Cyclohexylheneicosane (*l*)	−165.07	34.14
11-Phenylheneicosane (*l*)	−120.83	51.63

The tabulated value for the enthalpy of formation (ΔH^0_f) of ethylcyclohexane has been taken from the work of Prosen, Johnson and Rossini.[14] That for *n*-hexadecane has been computed from a molal heat of combustion of 2557.50 kcal., which value represents a weighted (6 to 1) mean of the combustion determinations of Prosen and Rossini[15] and of Richardson and Parks.[3] The ΔH^0_f values for the remaining hydrocarbons have been taken from the combustion studies of Parks and co-workers,[3,4,5] with appropriate revisions, where necessary, to the present-day standards.[16]

In general, the free energies as derived from these ΔH^0_f quantities and the ΔS^0_f values in Table IV are probably reliable to within 0.05 or 0.06 kcal. per carbon atom, although in one or two instances, including that of *n*-heptylcyclohexane, the error may be appreciably greater than these figures. In this connection it should be noted that such calculations of free energy put a much heavier requirement for accuracy upon the measurement of the heat of combustion than upon the evaluation of the entropy. For example, in the case of 11-*n*-decylheneicosane an error of 1% in the molal entropy amounts to 2.62 e. u. and corresponds to 0.78 kcal. in free energy, while a mere 0.03% error in the heat of combustion corresponds to 1.47 kcal.

On the basis of these tabulated free energies we have deduced 1.21 kcal. for the average change in molal free energy per CH_2 increment in the series of liquid normal paraffins and normal alkylcyclohexanes. Likewise, through these and other data we have arrived at 12.8 kcal. as the approximate contribution of the cyclohexyl group in a series of liquid straight-chain compounds.

Summary

1. The specific heats of nine hydrocarbons of high molecular weight have been measured between 78 and 300° K. The corresponding heats of fusion have also been determined in seven cases.

2. The entropies of these hydrocarbons in the liquid or crystalline states at 298.16° K. have been calculated from the foregoing heat capacity data, and certain structural contributions have been noted.

3. The corresponding molal free energies have also been calculated. From these and other data values of 1.21 kcal. and 12.8 kcal. have been deduced for the respective contributions of a CH_2 increment and a cyclohexyl group in liquid straight-chain compounds.

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[14] E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 51 (1946).

[15] E. J. Prosen and F. D. Rossini, *ibid.*, **33**, 255 (1944).

[16] R. S. Jessup, *ibid.*, **29**, 247 (1942).