263. *Melting-point and X-Ray Data for 2 : 4-Dinitrophenylhydrazones of n-Aliphatic Aldehydes.*

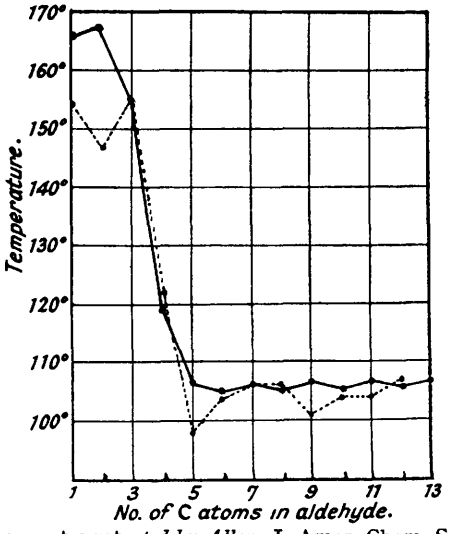
By T. Malkin and T. C. Tranter.

The melting points of 2 : 4-dinitrophenylhydrazones of *n*-aliphatic aldehydes from valeraldehyde upwards, lie within too narrow a range to afford a reliable means of identification. Long *X*-ray spacings are found to be suitable for this purpose.

The value of 2 : 4-dinitrophenylhydrazine as a reagent for carbonyl compounds is well known (cf. Wild, " Characterisation of Organic Compounds," Cambridge Univ. Press, p. 112) but, as Campbell has pointed out (*Analyst*, 1936, **61**, 391), care is required in its use, owing to the many discrepancies in the recorded melting points of its derivatives. Although Campbell revised many of the latter, he did not do so for the derivatives of *n*-aliphatic aldehydes, the melting points of which fall on an unusually irregular curve (Fig. 1). In view, therefore, of the value

Fig. 1.

M. p.s of 2 : 4-dinitrophenylhydrazones of n-aliphatic aldehydes.



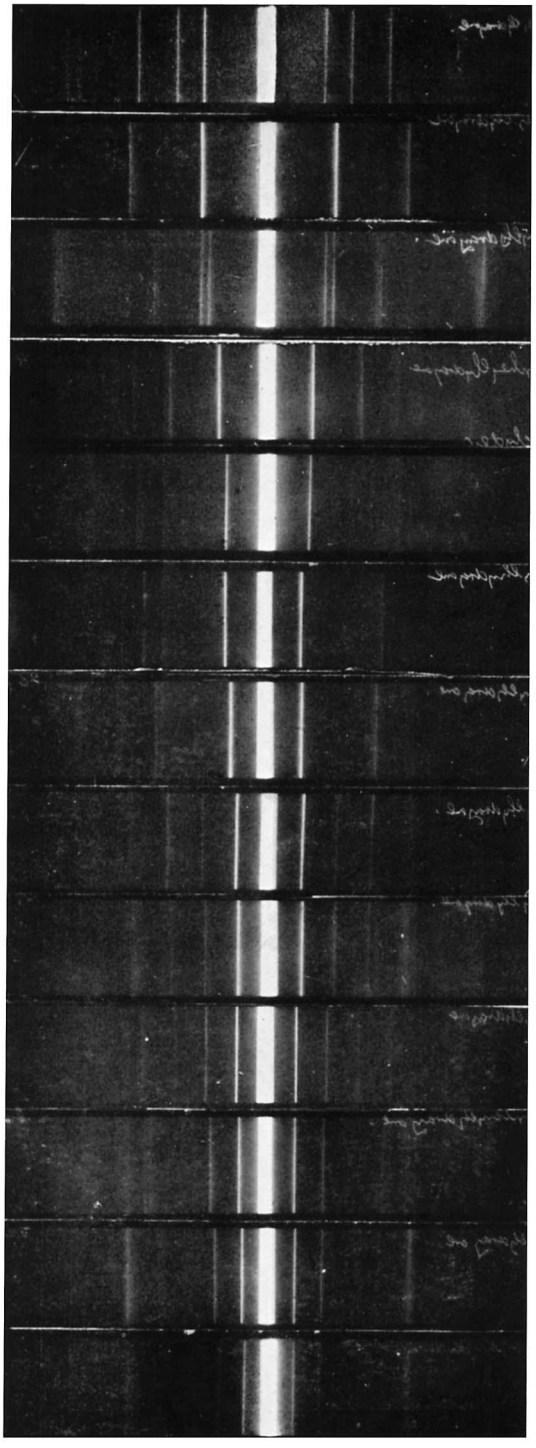
Discontinuous lines : m. p.s reported by Allen, J. Amer. Chem. Soc., 1930, **52**, 2955.

of a ready means of identification of these aldehydes, for example, in constitutional studies of unsaturated fatty acids, we have revised the melting points, using authentic aldehydes (Fig. 1; Table). These now show a more normal behaviour, but unfortunately the higher members

No. of C atoms in aldehyde.	M. p.	Long spacings, A.	Side spacings, A.								
1	166°	7·33, 10·38	3·09	—	3·48	3·64	—	—	—	—	—
2	167·5	9·40	—	3·25v	3·4	3·63	—	—	—	—	—
3	155	10·95, 9·64	—	3·26	3·42	—	—	—	—	4·40	4·74
4	119	13·5	—	3·27	3·37m	—	3·82	—	—	4·41m	—
5	106	15·08	—	3·25	—	3·66	3·78	—	—	—	—
6	105	16·34	—	3·25	—	—	3·72	—	4·15m	4·5m	—
7	106	17·78	3·21m	3·31	—	—	3·76	4·08m	4·17m	4·45	4·63
8	105·5	19·15	—	3·28	—	—	3·74	—	4·22	4·58	—
9	106·5	19·6	—	3·26	—	3·68	—	3·96m	—	—	4·72
10	106	21·12	—	3·26	—	3·69	—	3·95m	—	—	4·72
11	106·5	22·38	—	3·28	—	3·71	—	3·96	—	—	4·75
12	106	23·95	—	3·25	—	3·65	—	3·91	—	—	4·73
13	106·5	25·4	—	3·29	—	3·69	—	3·99	—	—	4·77

Only the strong spacings are recorded : m = moderately strong; v = very strong.

X-*Ray long spacings of the* 2 : 4-*dinitrophenylhydrazones of the normal aliphatic aldehydes.*



Formaldehyde.

Acetaldehyde.

Propaldehyde.

n-*Butaldehyde.*

n-*Valeraldehyde.*

n-*Hexanal.*

n-*Heptanal.*

n-*Octanal.*

n-*Nonanal.*

n-*Decanal.*

n-*Undecanal.*

n-*Dodecanal.*

n-*Tridecanal.*

[*To face p.* 1179.

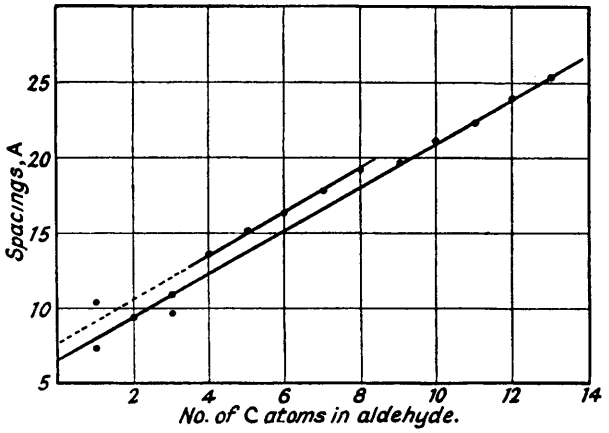
(from C_5 to C_{13} aldehydes) melt over a range of only 1·5°, and are thus of little value for purposes of identification. As, however, these derivatives have the advantage over most others in ease of preparation, we have, as an alternative method of identification, determined their *X*-ray spacings (Table; Fig. 2; and Plate). These fall on two parallel straight lines with a break indicating a slight change in structure between C_8 and C_9 (Fig. 2). Except for the last two, which differ by 0·45 A., the difference in spacings between homologues is $\simeq$1·4 A., which is well beyond any likely experimental error. Even with C_8 and C_9, where an intermediate value might give rise to doubt, the two are readily distinguished by the photographs (cf. differences in intensity of the lines, and the double line at the third order on C_9; see Plate), and should doubt still exist, the side spacings distinguish them decisively.

Experimental.

The dinitrophenylhydrazones were made by Brady's method (sulphuric acid and ethyl alcohol) (*J.*, 1931, 756), and crystallised from methyl alcohol. In agreement with Campbell (*loc. cit.*), we found benzene an unsatisfactory solvent, m. p.s being many degrees low after several crystallisations.

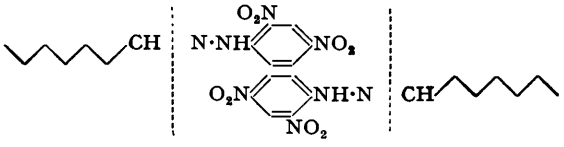
Fig. 2.

Long spacings of 2 : 4-*dinitrophenylhydrazones of* n-*aliphatic aldehydes.*



X-*Ray Investigation.*—A Müller spectrograph was used with a Metalix *X*-ray tube (Cu-K_α, λ = 1·54 A.) running at $\simeq$10 ma., distance of specimen from film, 6 cm. Long spacings were obtained from pressed layers, and side spacings from rods (see *J.*, 1936, 1631) or from loosely packed capillaries of goldbeater's skin. Exposures of ¼ hour for rods, or of ½ hour each side of centre for layers, were adequate.

The increment per carbon atom of 1·4 A. indicates a structure of layers of double molecules, tilted at an angle of about 34° to the reflecting planes (an increment of 1·26 A. per carbon atom being assumed for a vertical zig-zag hydrocarbon chain). The intercepts at 0 carbon atom (Fig. 2) of 6·5 A. and 7·6 A., respectively, for the two forms, would suggest an almost complete overlap of the aromatic heads of the double molecule, *viz.*



This would not be inconsistent with the spacing of 5·89 A. found for 2 : 4-dinitrophenylhydrazine itself, which might well crystallise in the head-to-tail arrangement indicated above, between the dotted lines.

During our investigation, we confirmed the results of Miss F. O. Bell (*Biochem. J.*, 1941, **35**, 312), who gave *X*-ray evidence for the dimorphism of the 2 : 4-dinitrophenylhydrazone of acetaldehyde, noted earlier by other workers (Bryant, *J. Amer. Chem. Soc.*, 1933, **55**, 3201; Ingold, Pritchard, and Smith, *J.*, 1934, 86), and it is hoped shortly to publish details of the structures of the two forms.

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