

Melting-point diagram and spectra confirm that commercial diphenylcarbazone is an 1:1 intermolecular compound of diphenylcarbazide and pure diphenylcarbazone. Methods of separation by continuous liquid-liquid extraction and thin-layer chromatography are proposed. Some physical and chemical properties of diphenylcarbazone and of its reduced and oxidised forms, diphenylcarbazide and diphenylcarbadizone, respectively, are reported.

STUDIES WITH DIPHENYLCARBAZONE.

I. PURIFICATION AND CHARACTERIZATION OF DIPHENYLCARBAZIDE, DIPHENYLCARBAZONE AND DIPHENYLCARBADIAZONE

J. J. R. FRAÚSTO DA SILVA
J. C. CONÇALVES CALADO
M. LEGRAND DE MOURA

Centro de Estudos de Química Nuclear (I. A. C.)
Instituto Superior Técnico — Lisboa

1 — INTRODUCTION

1.1. Diphenylcarbazone has not found in analytical chemistry a prominent position like its sulphur analogue diphenylthiocarbazone or «dithizone», but its reduced form, diphenylcarbazide, is a widely used reagent for chromium which has aroused general attention. However, the reactions of both compounds with metals are not very well understood, and have originated many contradictory reports (1-8).

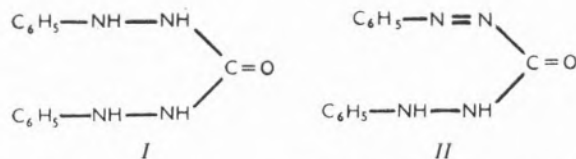
Some of the discrepancies result from the fact that various workers used the commercially available AnalaR products without any further purification; this is utterly important, as found by other investigators, and a thorough characterization of the reagents is necessary for the rigorous control of their purity before undertaking any studies on complex-formation.

In the present paper new methods of purification are described and data are given for the complete and unambiguous characterization of the pure compounds.

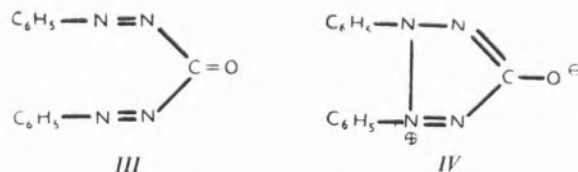
1.2. Diphenylcarbazide (1,5-diphenylcarbohydrazide) — as I — is a white crystalline solid, melting at 172-3°C when recently recrystallized. It is almost insoluble in water but slightly soluble in several organic solvents such as acetone, ethyl-ether, chloroform, ethanol, etc.

Oxidation of diphenylcarbazide with hydrogen peroxide in alcoholic potassium hydroxide (1) gives an

orange product which can be recrystallized from aqueous ethanol being obtained in needles m. p. 157°C. This product was thought to be diphenylcarbazone (1,5-diphenylcarbohydrazone) — as II — but KRUMHOLZ and KRUMHOLZ showed that it was, in fact, a 1:1 mixture or an intermolecular compound of diphenylcarbazide and diphenylcarbazone m. p. = 127°C which they succeeded in separating (9)



Oxidation of diphenylcarbazide with a silver salt (1) or isoamylinitrite (10) gives a white product slightly soluble in ethanol and water which explodes at about 160°C. This product is known as diphenylcarbadizone — III — and BAMBERGER suggests that it should be formulated as IV, e. g. in the betaine form (10)



This behaviour is established beyond any doubt; yet, the product available nowadays as AnalaR diphenylcarbazone is still the 1:1 mixture, recognisable by its melting point at 157°C, and studies carried on with this compound as such cannot be correct.

As to diphenylcarbazide various commercial products of variable degrees of purity are available, requiring repeated recrystallizations and immediate use. In some cases recrystallizations did not improve sufficiently the purity and those particular brands had to be abandoned.

On the other hand, solutions of diphenylcarbazide in some solvents do not keep very well, as clearly demonstrated by URONE (11), and the same happens with the solutions of diphenylcarbazone. This may be another cause for the discrepancies in the literature.

Several investigators used diphenylcarbazone purified by KRUMHOLZ's method (9); details of the procedure are not given and the properties indicated for the pure product are very scarce and rather confusing. Only for the melting point does agreement appear to be general; this, in a way, is surprising, because of the closeness of the eutectic melting at lower temperature, as will be shown below.

The consideration of diphenylcarbadiazone is due to the fact that it frequently is one of the products of the reactions of diphenylcarbazide and diphenylcarbazone with metals; the detection of that product is then a fundamental step for the understanding of the mechanism of those reactions.

Furthermore, the compound itself offers a challenging structural problem which remains to be solved, and a more detailed investigation of its properties seemed of interest.

2 — EXPERIMENTAL

2.1 — REAGENTS

2.1.1 — Diphenylcarbazide

The commercial product was dissolved in boiling ethanol, and water was added dropwise until permanent turbidity. On cooling, the reagent separated in small crystals which were collected, rapidly washed with iced ethyl-ether, and dried at 50°C for a few minutes. The operation was repeated if necessary until the product melted at 172-3°C. The yield varied with the brand, being of the order of 90 % for the best.

2.1.2 — Diphenylcarbazone

This reagent was purified by a continuous liquid-liquid extraction method which was developed to prepare relatively substantial amounts of the product.

The procedure was already given elsewhere (12) and simply consists in adapting KRUMHOLZ's instructions (9) to continuous operation.

An extractor similar to that used by ASHLEY and MURRAY for the extraction of FeCl_3 with ether (13) appeared to be best suited for the purpose and excellent results were indeed obtained with it — fig 1.

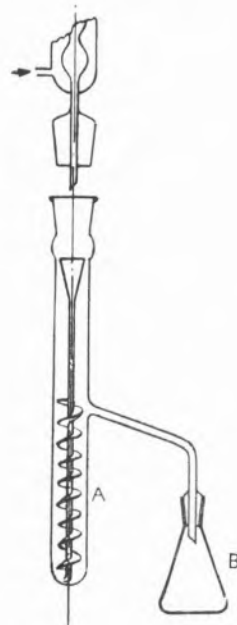


Fig. 1 — Extractor used for the continuous liquid-liquid separation of diphenylcarbazide and diphenylcarbazone.

The commercial AnalR product was dissolved in a hot solution of NaOH containing a few miligrams of KCN; diphenylcarbazone, being an acid, will be in solution in its anionic form, contrarily to diphenylcarbazide which has no acidic character. If this solution is extracted with an organic solvent in which diphenylcarbazide is soluble, this compound will be separated from diphenylcarbazone which remains in the aqueous phase. Ether was the solvent of choice. For the extraction ether was placed in flask B of the extractor and the caustic aqueous solution, after being filtered, was placed in tube A. By refluxing the organic solvent, extraction was allowed to proceed for about 24 hours.

Diphenylcarbazide is carried into the Erlenmeyer flask B where it crystallizes in long colourless needles. Diphenylcarbazone is precipitated by acidification of the alkaline solution left in A; recrystallization of the product with aqueous ethanol gives the pure compound in small orange-red needles m. p.

125-7°C (rapid heating). The yield was of the order of 40 % (first crystallisation).

Good separations were also achieved by thin layer chromatography as we described elsewhere (12). This is a different and independent method and the results obtained by KRUMHOLZ and KRUMHOLZ are thus supported.

2,1,3 — Diphenylcarbadiazone

Diphenylcarbadiazone was prepared by a modified procedure according to CAZENEUVE (14) : 2.4 g of commercial diphenylcarbazon (0.005 moles of diphenylcarbazon and 0.005 moles of diphenylcarbazon) were dissolved in ethanol (50 ml) and added with energetic stirring to 5.0 g of silver acetate (0.03 moles) in about 400 ml of boiling water.

The mixture was boiled for a further fifteen minutes and filtered to separate metallic silver formed in the reaction. The resulting yellow solution was treated with activated charcoal and concentrated by distillation under reduced pressure. Diphenylcarbadiazone, which precipitated in the flask, was collected and recrystallized from water, yielding 1.07 g of white crystals which explode at 180°C.

2,2 — GENERAL DETAILS

All chemicals used in this work were of AnalaR grade; solvents were further purified by standard methods (15).

All the glassware was previously washed with a concentrated solution of EDTA and then rinsed with deionised water.

The solvents were freed from oxygen by bubbling nitrogen through for 30 minutes before preparing any solutions. These were kept in stoppered flasks, usually in darkness, and used within periods of few hours.

UV and visible spectra were recorded in the Bausch & Lomb «Spectronic 505» spectrophotometer; IR spectra in the Perkin-Elmer spectrophotometer model 21, with NaCl prism and using KBr pellets.

Melting points were obtained by the Thiele tube method and are uncorrected.

3 — RESULTS AND DISCUSSION

The methods described yielded the compounds in excellent state of purity: in the case of diphenylcarbazon, better samples were obtained using the

present method than when using KRUMHOLZ's batch extraction technique.

Pure diphenylcarbazon is a deep orange crystalline powder, not *red* as quoted before; it is easily soluble in ethanol, chloroform and methylene dichloride and rather more difficultly in acetone, ether, benzene and carbon tetrachloride, up to concentrations of the order of 10^{-3} M; when rapidly heated it melts at 125-7°C.

Diphenylcarbazon melts at 172-3°C only when recently recrystallized; after some time the reagent is

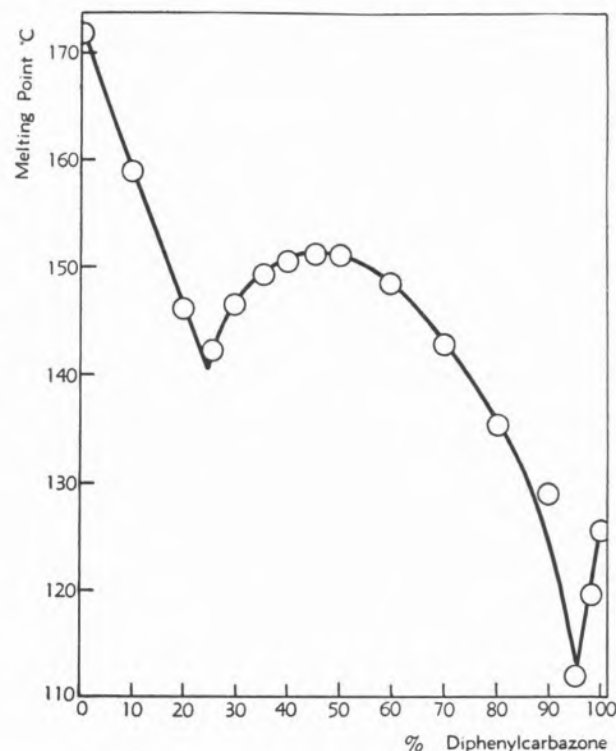


Fig. 2 — Melting-point diagram for equimolecular mixtures of diphenylcarbazon and diphenylcarbazon.

oxidised, even in the solid state, and its melting-point sinks progressively.

A melting-point diagram for equimolecular mixtures of diphenylcarbazon and diphenylcarbazon shows the behaviour already noticed by KRUMHOLZ and KRUMHOLZ (9) — fig. 2.

For mixtures rich in diphenylcarbazon there is a sharp decrease in melting point down to about 140°C due to the formation of an eutectic with 20-25 % of this compound. Melting points then rise up to a maximum at 50 % composition and fall slowly afterwards to another probable eutectic with 3-5 % diphenylcarbazon which melts at about 110°C. Pure

diphenylcarbazone melts at 125-7°C as mentioned before.

The maximum at 50% indicates the formation of a 1:1 intermolecular compound of diphenylcarbazide and diphenylcarbazone, as expected from the behaviour of the commercial product which can withstand successive recrystallizations without changing composition. The melting point of the maximum is lower than that of the pure intermolecular compound (157°C); this is due to the energy of formation of the dimer which involves some kind of bonding. Several samples of «purified» diphenylcarbazone were obtained melting at temperatures between 112-126°C. This agrees with the existence of the expected eutectic, rich in diphenylcarbazone and very close to it in the diagram. Using calculated extinction coefficients it is possible to estimate that this eutectic has 3-5% diphenylcarbazone; the limited accuracy of melting point data does not allow more rigorous conclusions.

The existence of a quite stable intermolecular compound of diphenylcarbazide and diphenylcarbazone suggests that relatively strong bonding exists between

at all. It is only in aqueous alkaline solution that either complete dissociation occurs or the bonds are weakened to an extent that allows separation by extraction to be feasible. Consistent with the first hypothesis is the fact that determinations of the molecular weight of the dimer by an isopiestic method did not give evidence for associated species.

To characterize the pure compounds now obtained

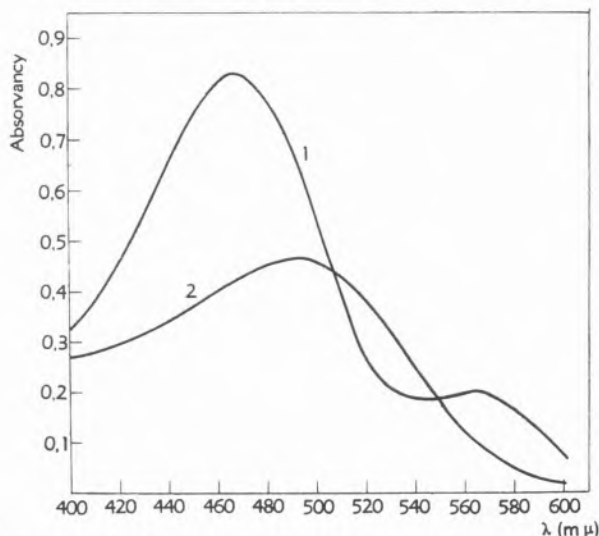


Fig. 4 — Visible spectra of diphenylcarbazone in carbon tetrachloride (1) and ethanol (2). Concentration 2.5×10^{-4} M.

and to get some information on their structure, UV, visible and IR spectra were recorded and are presented in figs. 3, 4 and 5.

The wavelength of maxima of absorption in UV and visible spectra and the respective molar extinction coefficients are summarized in table 1.

BALT and VAN DALEN, who recently started a systematic study of diphenylcarbazone metal complexes (16) and purified their reagent by KRUMHOLZ's method, reported values for ϵ_{\max} close to ours but not quite so high, even if the error limits indicated are taken into account (17).

UV and visible spectra of these compounds have been briefly discussed by GRAMMATICAKIS (18) who concluded that in alcoholic solution diphenylcarbazone resembles azo compounds and differs from formazans, so that in the possible tautomeric equilibrium between the ketonic and enolic forms the first is predominant. BALT and VAN DALEN found, on the other hand, that in toluene and carbon tetrachloride the carbazone resembles the formazans more than it does in aqueous or alcoholic solutions (17); this was taken to indicate that in those solvents a considerable part of

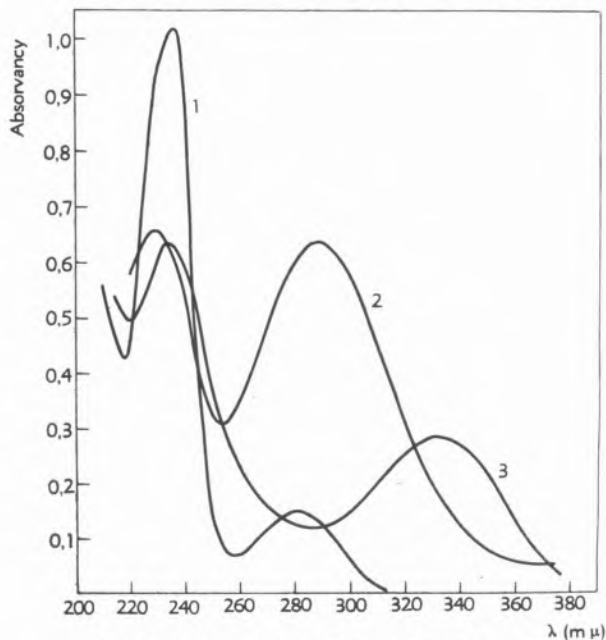


Fig. 3 — UV spectra of diphenylcarbazide (1) diphenylcarbazone (2) and diphenylcarbadiazone (3) in ethanol. Concentration 5×10^{-5} M.

the two molecules. It is worth pointing out that an attempted separation of the components by exhaustively extracting the solid sodium salt of the commercial product with organic solvents did not succeed

Table I

Compound	Solvent	λ_{max} m μ	ϵ_{max} cm ⁻¹ mol ⁻¹
Diphenylcarbazone	Ethanol	230	13 150
		285	12 800
		490	1 870
	Carbon tetrachloride	290	13 500
		466	3 300
		563	800
Diphenylcarbazide	Ethanol	236	20 400
		286	2 990
Diphenylcarbadiazone	Ethanol	233	12 700
		330	5 800

the carbazone is present in the enolic form, and the authors accordingly suggested that the absorption at 560 m μ in carbon tetrachloride is probably due to the ketonic form of diphenylcarbazone.

The difference in behaviour certainly results from the fact that in alcoholic or aqueous solutions the lone pair of electrons in the carbonyl oxygens may be donated to the hydroxylic atom of the solvents, thus forming hydrogen bonds and stabilising the keto-tautomer.

Similar behaviour has been found in other cases of tautomeric equilibria (19).

IR spectra (fig. 5) which were obtained in KBr pellets, do not give much information on the structure of the compounds under consideration.

A complete discussion of these spectra is a matter of great difficulty, as for other urea derivatives, and will not be attempted. Only a few points will be briefly considered.

The spectrum of the intermolecular compound of diphenylcarbazide and diphenylcarbazone (a) is almost the superimposition of the individual spectra of these reagents (b, c). There is no evidence for special bonds but there is a new band at 865 cm⁻¹ which could not be identified.

The —NH stretching frequency is located at 3280 cm⁻¹, as in several other cases of hydrogen bonded amides (20) but it is not clear whether intramolecular or intermolecular bonds are involved.

The same is verified in the spectra of pure diphenylcarbazone and of diphenylcarbazide, but in the latter a sharp band at 3440 cm⁻¹ indicates free —NH groups.

The carbonyl stretching frequency in the spectrum of diphenylcarbazide is found at 1660 cm⁻¹ and in

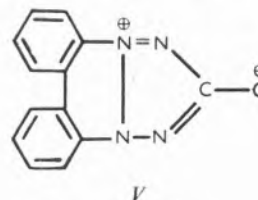
the cases of pure diphenylcarbazone and of diphenylcarbadiazone there are also bands at 1700 cm⁻¹ and 1655 cm⁻¹ which may correspond to carbonyl stretching frequencies; however, since the —C=N vibration may occur in the same position, the assignment is rather ambiguous.

On the other hand, —C—O— bands could not be precisely identified; it is likely that the vibrations at 985 cm⁻¹ in pure diphenylcarbazone and 988 cm⁻¹ in diphenylcarbadiazone correspond to stretching frequencies of this group, but no absolute proof can be given.

For the same substances a band at 928 cm⁻¹ is probably due to the grouping —C=N=N—C—, as suggested by TETLOW for some azo compounds (21); in the case of diphenylcarbadiazone a shoulder at 1626 cm⁻¹ can be ascribed to —N=N— stretching (22) and the splitting of bands at 750-790 cm⁻¹ may indicate a *cis*— structure relatively to the double —N=N— bond.

Unfortunately, these results are too vague to support reasonable hypothesis on the structure of the compounds studied.

For diphenylcarbadiazone, the betaine form suggested by BAMBERGER (10) seems likely, on the basis of the physical properties of the product (colour, explosive character, reduced solubility in non-polar solvents, etc.). Furthermore its solutions are sensitive to UV light turning yellow with time, probably due to the formation of (2,2'-diphenylene)-5-oxitetrazolium betaine —V—, similarly to what happens with other tetrazolium salts (23).



However, the IR spectrum of diphenylcarbadiazone is perhaps more easily understood in terms of the «diazone» structure and no conclusive evidence can be taken from the bands between 9 and 10 μ , which characterize the tetrazole ring, as suggested by LIEBER and col. (24). If a mesomeric form is accepted for the structure of this compound, this may imply the predominance of «diazonic» forms since the presumed carbonyl stretching is not shifted relatively to the frequency found in diphenylcarbazide.

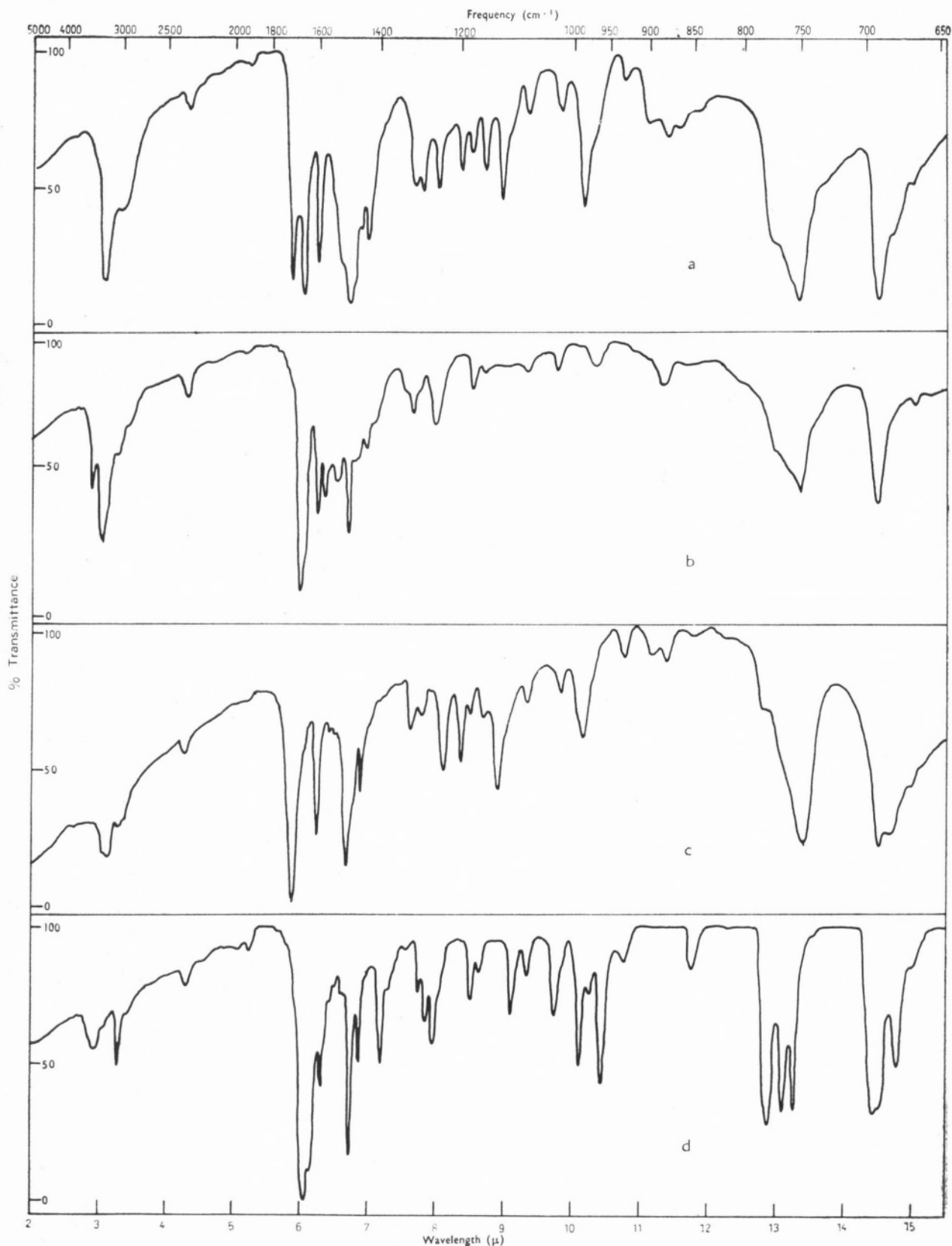
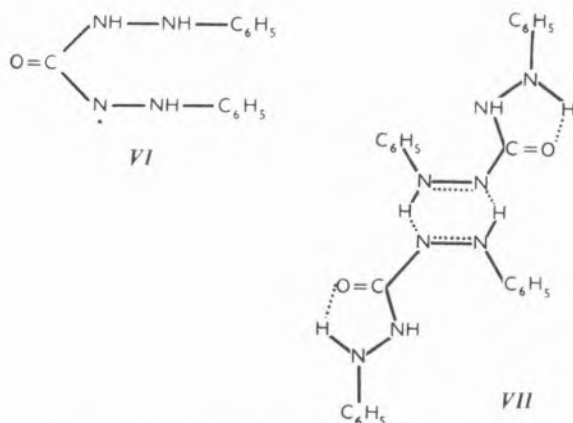


Fig. 5—IR spectra of commercial diphenylcarbazone (a), diphenylcarbazide (b), diphenylcarbazone (c) and diphenylcarbadiazone (d) in KBr pellets.

For diphenylcarbazone in the solid state the keto-form is again more likely and the same is true, of course, for diphenylcarbazide.

The structure of the intermolecular compound of diphenylcarbazide and diphenylcarbazone could not be elucidated by the spectra. We think that it derives from the free radical VI, which may be formed in the first stage of mild oxidation of diphenylcarbazide; if this is the case, hydrogen bonds may be established between nitrogen atoms, as in VII, but these would not be revealed in the IR spectrum because their vibrations would be merged with the —CH vibrations at 3000 cm⁻¹.



The structure suggested cannot be proved; however it explains why mild oxidation of diphenylcarbazide stops at the 1:1 intermolecular compound, leaving exactly 1/2 of the diphenylcarbazide without being oxidized. This is, indeed, an intriguing feature of the reaction and the obvious conclusion is that the symmetrically placed nitrogen atoms of the intermolecular compound are in some way equivalent, as in VII.

More work is necessary for complete elucidation of these problems; NMR spectra will certainly help if solubility difficulties can be overcome, but their interpretation is likely to be still very difficult. Nevertheless, the characterization and control of purity of diphenylcarbazide, diphenylcarbazone and diphenylcarbadiazone, which was the main purpose of our work, is now easily feasible by means of the specified properties and spectra of the compounds. In particular, the UV spectrum of diphenylcarbadiazone shows a maximum of absorption at 330 mμ, which allows the detection and determination of the compound in the presence of diphenylcarbazide and diphenylcarbazone. This is important when studying

the reactions of the latter with metals, because it enables one to verify if oxidations of the reagents did in fact occur.

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RESUMO

Confirma-se, com base no diagrama de pontos de fusão e espectros no infra-vermelho, que a difenilcarbazona p.a. comercial é uma associação intermolecular de difenilcarbazona pura e de difenilcarbazida, nas proporções 1:1. Propõem-se novos métodos de separação da difenilcarbazona por extracção contínua líquido-líquido e por cromatografia em camada fina. Indicam-se algumas propriedades físicas e químicas da difenilcarbazida e da difenilcarbazona pura, assim como do seu produto de oxidação, a difenilcarbadiazona, e discute-se a estrutura destes compostos a partir dos espectros no visível, no ultravioleta e no infravermelho.

REFERENCES

1. Cazeneuve, P., *Bull. Soc. Chim. France*, **25**, 758 (1901).
2. Feigl, F., «Chemistry of Specific, Selective and Sensitive Reactions», Academic Press, New York, 1949, p. 241.
3. Babko, A. K. and Palii, L. A., *Zh. Analit. Khim.*, **5**, 272 (1950).
4. Bose, M., *Anal. Chim. Acta*, **10**, 201 (1954).
5. Bose, M., *Anal. Chim. Acta*, **10**, 209 (1954).
6. Pflaum, R. T. and Howick, L. C., *J. Am. Chem. Soc.*, **78**, 4826 (1956).
7. Das Sarma, B. and Ray, J. N., *Sci. Cult. (Calcutta)*, **21**, 477 (1956).
8. Lichtenstein, I. E. and Allen, T. L., *J. Am. Chem. Soc.*, **81**, 1040 (1959).
9. Zittel, H. E., *Anal. Chem.*, **35**, 329 (1963).
10. Krumholz, P. and Krumholz, E., *Monatsh.*, **70**, 431 (1937).
11. Bamberger, E., Padova, R. and Ormerod, E., *Ann. Chem.*, **446**, 260 (1926).
12. Urone, P., *Anal. Chem.*, **27**, 1354 (1955).
13. Silva, J. J. R. F. da, Calado, J. C. G. and Moura, M. L. de, *Talanta*, **11**, 983 (1964).
14. Ashley, S. E. and Murray, W. M., *Ind. Eng. Chem. (Anal. Edition)*, **10**, 367 (1938).
15. Cazeneuve, P., *Bull. Soc. Chim. France*, **25**, 375 (1901).
16. Schefflan, L. and Jacobs, M., «The Handbook of Solvents», D. Van Nostrand, New York, 1953.
17. Balt, S., «Dissertation», Amsterdam, 1962.
18. Balt, S. and Van Dalen, E., *Anal. Chim. Acta*, **25**, 507 (1961).
19. Grammaticakis, P., *Compt. Rend.*, **234**, 528 (1952).
20. Rao, C. N. R., «Ultraviolet and Visible Spectroscopy», Butterworths, London, 1961, p. 70.
21. Bellamy, L. J., «The Infrared Spectra of Complex-molecules», Methuen & Co., London, 1958, p. 207.
22. Tetlow, K. S., *Research (London)*, **3**, 187 (1950).
23. Meites, L., «Handbook of Analytical Chemistry», McGraw-Hill, New York, 1963, p. 6-140.
24. Nineham, A. W., *Chem. Rev.*, **55**, 355 (1955).
25. Lieber, E., Levering, D. R. and Patterson, L. J., *Anal. Chem.*, **23**, 1594 (1951).