

For the remaining eight substances there are available in the literature a fair number of early values, mostly obtained around 1890, and a few really modern results. The early values¹³ include determinations on all eight substances by Stohmann and his collaborators and a few results by Luginin and by Berthelot. Today it is practically impossible to translate these early data over to our modern standards. As published, they tend to run higher than our present results by amounts ranging up to 1.4%.

Coming to the modern data, where it is possible to put the heats of combustion on a better comparative basis with our new values, we find that Beckers¹⁴ results for cetyl alcohol and anthracene differ from ours by only -0.05 and $+0.02\%$, respectively, the values of Verkade and Coops¹⁵ for phthalic acid and phthalic anhydride exceed ours by 0.02 and 0.51%, and that of Swietoslawski¹⁵ for phthalic anhydride is 0.04% above our result. In the case of stilbene Roth's value¹³ exceeds the present result by 0.17%, that of Berner¹⁶ by 0.07%. For phenanthrene other recent values¹⁷ differ from that given here by -0.06 and

$+0.45\%$, and correspondingly for anthracene by $+0.03$ and $+0.17\%$. For triphenylbenzene Professor Huffman at the California Institute of Technology has kindly made a pair of determinations on our original material with his own calorimetric apparatus. His mean result is 0.02% above that reported in this paper.

Acknowledgment.—Before concluding, we wish to thank Professor H. M. Huffman for his valuable advice and aid so generously given on many occasions during this investigation. We also desire to acknowledge our indebtedness to Mr. George E. Moore for purifying the samples of *n*-hexadecane and cetyl alcohol and making several of the combustions on these materials.

Summary

1. A bomb calorimeter has been calibrated and then used for precise measurements of the heats of combustion of the following eleven substances at 25° and constant volume: β -methyl-naphthalene, phthalic anhydride, phthalic acid, anthracene, phenanthrene, stilbene, pyrene, *n*-hexadecane, cetyl alcohol, triphenylbenzene and polyisobutylene.

2. From these experimental results the corresponding heats of combustion and heats of formation at constant pressure have been calculated.

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RECEIVED SEPTEMBER 12, 1939

- (13) Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1587.
 (14) Beckers, *Bull. soc. chim. Belg.*, **40**, 518 (1931).
 (15) Verkade and Coops, *Rec. trav. chim.*, **47**, 606 (1928).
 (16) Berner, *Arch. Math. Naturvidenskab*, **39**, No. 6 (1926).
 (17) Milone and Rossignoli, *Gazz. chim. ital.*, **62**, 644 (1932); Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES, ARMOUR INSTITUTE OF TECHNOLOGY]

Raman Spectra of Acetylenes. II. Displacements and Depolarization Factors for Phenylacetylene and Derivatives of the Type $C_6H_5C\equiv CR^1$

BY M. J. MURRAY AND FORREST F. CLEVELAND

As was indicated in the first paper of this series² (subsequently referred to as I) the line near 2200 $cm.^{-1}$ in disubstituted acetylenes is not single, but is split into two or more parts. To explain this doubling, Gredy³ postulates the co-existence of two molecular forms each of which gives its own characteristic frequency. Kohlrausch, Pongratz and Seka⁴ give some support to this hypothesis by the statement that more than one

frequency, if only one molecular form is present, is difficult to understand. Badger⁵ attributes the splitting to a Fermi resonance interaction between the fundamental in this region and an overtone of a frequency near 750 or 1100 $cm.^{-1}$, the latter of which should not appear in the Raman spectra. Glockler and Davis⁶ accounted for the two lines in dimethylacetylene by supposing that one is due to a symmetrical, the other to an asymmetrical, vibration. If this is true for disubstituted acetylenes in general, the two frequencies in this region should have strikingly

- (1) Much of the experimental work discussed in this paper was carried out at Lynchburg College.
 (2) M. J. Murray and Forrest F. Cleveland, *THIS JOURNAL*, **60**, 2604 (1938).
 (3) Blanche Gredy, Thèses, Paris, 1935.
 (4) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Sitzber. Akad. Wiss. Wien., Abt. IIb*, **146**, 218 (1937).

- (5) R. M. Badger, *J. Chem. Phys.*, **5**, 178 (1937).
 (6) G. Glockler and H. W. Davis, *ibid.*, **2**, 881 (1934).

different depolarization factors. The present investigation was designed to test this point with a number of available derivatives of phenylacetylene.

Experimental Procedure

The method used in determining the depolarization factors has been described elsewhere.⁷ Since the spectra of phenylacetylene derivatives are more intense than those of the compounds therein measured, it was possible to decrease the slit width (thus giving better resolution) and to reduce to ninety minutes the time for each exposure.

The Raman frequencies of several of these compounds were reported in I.² Since in the present investigation a superior filter⁸ and a spectrograph⁷ having better optical parts and greater dispersion were used, it has been possible to obtain some of the frequencies with a greater degree of certainty than before. This remark applies especially to the frequencies near 3000 cm.⁻¹. Much of the improvement in this region, however, is due also to the use of a different photographic emulsion (Agfa Super Plenachrome Press) which was more sensitive to the green wave lengths. Since the acetylenic compounds used undergo photochemical decomposition rapidly when exposed to light of short wave length and since the filter used was exceedingly efficient in isolating Hg 4358 Å., it was necessary and desirable to use only this frequency for excitation. For example, with this filter the strongest line in the spectra (the 2200 cm.⁻¹ line) did not appear on the spectrograms as excited by Hg 4047 Å. Furthermore, all the mercury lines near 5000 Å. were completely eliminated by the filter except Hg 4916 Å. and Hg 4960 Å. which were severely weakened, the latter being observable with great difficulty on long exposures.

In certain cases, noted in the data, the material available was insufficient to fill the Raman tube, and it was necessary to add carbon tetrachloride. Experience proved that this had no observable effect upon the spectra. In a few instances where a carbon tetrachloride line chanced to coincide with one of the lines of the acetylenic compound, it was impossible to read the depolarization factor.

Results

In the tabulation of results the displacement in cm.⁻¹ is written first, followed by the estimated intensity in parentheses, which in turn is followed by the depolarization factor, except in cases where low intensity or other cause prevented its measurement. Lines which are unusually broad are designated by the letter b following the intensity notation. Data in regard to which there is some uncertainty are enclosed in brackets. Frequencies which were observed both as Stokes and anti-Stokes lines are designated by the sign =. In the case of those compounds studied in I,² the present

tabulation includes those frequencies for which depolarization factors have now been obtained, frequencies which have been redetermined with greater precision, and some frequencies not previously observed. Each new or revised value is indicated by an asterisk. The present estimated intensities are regarded as somewhat more reliable than those reported in I.² Because of improvements in technique given above which greatly facilitate measurement in the 3000 cm.⁻¹ region, the present values of frequencies above 2800 cm.⁻¹ should replace in entirety those given in I.²

1. **Phenylacetylene** (C₆H₅C≡CH).—Synthesized from bromostyrene,⁹ b. p. 142°; previous data, Bourguel,¹⁰ and Bourguel and Daure.¹¹

$\Delta\nu = \pm 164(6).9; \pm 353(4).9; \pm 465(3)<.7; 517(2); \pm 530(3).9; 621(4b).9; 760(5).5; 1001(7).2; 1027(2)<.6; 1155(2); 1176(4).5; 1196(6).4; 1230(1); 1281(1); 1337(1); [1380(1)]; 1447(1); 1489(2b); 1601(9).8; 2113(10).6; 3066(8).5; 3142(1); 3288(3).$

2. **1-Phenylpropyne-1** (C₆H₅C≡CCH₃).—Synthesized by action of dimethyl sulfate on sodium phenylacetylide in ether solution, b. p. 72–73° (15 mm.); previous data, Gredy,¹² Bourguel,¹⁰ and Bourguel and Daure.¹¹

$\Delta\nu = 149(2); 298(3).8; 388(4).7; 401(2); 510(1); 528(3).9; 626(3); 701(3); 758(2); 953(1); 971(6).3; 1001(7).3; 1030(2); 1053(1/2); 1160(4) \text{ and } 1181(4)<.5; 1245(1); 1262(8).3; 1286(2); 1328(1); 1382(4b).9; 1436(3) \text{ and } 1450(3).7; 1489(4) \text{ and } 1500(4).7; 1601(9).7; 2214(9).6; 2231(4); 2246(10) \text{ and } 2262(6).6; 2913(4) \text{ and } 2930(3).4; 2955(1); 3066(4b).6; 3111(1); 3143(1).$

2231 was measured on three different spectrograms, but only when the camera lens was diaphragmed to 1.0 cm. did 2246 and 2262 appear resolved.

3. **1-Chloro-2-phenylethyne** (C₆H₅C≡CCl).—Synthesized by action of *p*-toluenesulfonyl chloride on sodium phenylacetylide, b. p. 73° (16 mm.); previous data, Bourguel and Daure.¹¹ Carbon tetrachloride added.

$\Delta\nu = 284(4); 334(3); 364(5).9; 500(2); 521(4); 619(3); 654(1); 754(2); 882(4); 1000(8).3; 1161(3); 1175(3); 1208(1); 1224(2); 1248(6).4; 1487(2); 1599(8).7; 2203(2); 2222(10).6; 3065(3) \text{ and } 3079(2)<.8.$

4. **3-Chloro-1-phenylpropyne-1** (C₆H₅C≡CCH₂Cl).—Carbon tetrachloride added; for previous data, see I.²

$\Delta\nu = 690(6b).5; 718(4).9; 980(7).4; 1006(2)<.9; 1159(3) \text{ and } 1174(3).8; 1251(8).5; 1491(4)<.9; 1600(9).8; 2214(10) \text{ and } 2231(10).7; 2263(4).7; 2956(3).6; 3064(5).6.$

5. **3-Phenyl-2-propynol-1** (C₆H₅C≡CCH₂OH).—For previous data, see I.²

$\Delta\nu = \pm 188(4b).9; \pm 270(3) \text{ and } 282(3).9; 366(3) \text{ and } 382(5).6; 530(5).7; 573(4).9; 625(5).7; 713^*(4).7; 756^*(5).8; 956(6).3; \pm 1000(8).2; 1023^*(4) \text{ and } 1038^*(2).3; 1158^*(4).9; 1179(5).6; 1258(7).4; 1447^*(4b).7; 1490^*(5).6; 1603(9).7; 2202(6).6; 2242(10).7; 2278^*(2); 2300^*(2); 2433^*(1); 2510^*(1); 2555^*(2); 2868^*(4)<.6; 2914^*(5) \text{ and } 2935^*(4).5; 3061(7).5.$

(7) Forrest F. Cleveland and M. J. Murray, *J. Chem. Phys.*, **7**, 396 (1939).

(8) J. T. Edsall and E. B. Wilson, Jr., *ibid.*, **6**, 124 (1938). The present authors have approximately doubled the strength recommended.

(9) "Org. Syntheses," Coll. Vol. I, 1932, p. 428.

(10) M. Bourguel, *Compt. rend.*, **195**, 311 (1932).

(11) M. Bourguel and P. Daure, *Bull. soc. chim.*, **47**, 1349 (1930).

(12) B. Gredy, *Compt. rend.*, **196**, 1119 (1933).

6. **3-Bromo-1-phenylpropyne-1** ($C_6H_5C\equiv CCH_2Br$).—Carbon tetrachloride added; for previous data, see I.²

$\Delta\nu = 609(2b).6; 887(6).4; 1206(5).6; 1269(3).8; 1599(8).7; 2226(10).6; 2265(4).6; 2950^*(3)<.6; 3064(5).4.$

7. **1-Phenylbutyne-1** ($C_6H_5C\equiv CCH_2CH_3$).—Synthesized by action of sodium phenylacetylide on ethyl *p*-toluenesulfonate, b. p. 83° (9 mm.); for previous data, see Gredy.¹²

$\Delta\nu = 180(2b).8; 383(3).7; 528(2)$ and $539(3).7; 624(2).9; 694(1).9; 757(2).9; 893(3)<.6; 999(8).3; 1016(2); 1069(1); 1161(3).7; 1184(4).6; 1240(2)$ and $1258(6).5; 1330(1).9; 1384(1).8; 1438(1b).8; 1493(2).7; 1599(8).8; 2206(4).7; 2238(10).7; 2839(1)<.7; 2914(3).6; 2931(3)[.3]; 2978(1b).9; 3061(5).6.$

A few of Gredy's assignments appear open to some question: 470 e (e = Hg 4358 Å.) is probably 2238 k (k = Hg 4047 Å.).¹³ 942 e, reported as a strong line by Gredy, appeared with small intensity and is likely 999 f (f = Hg 4347 Å.). 3025 k is probably 1258 e and 2944 k is probably 1177 e.

8. **4-Chloro-1-phenylbutyne-1** ($C_6H_5C\equiv CCH_2CH_2Cl$).—Carbon tetrachloride added; for previous data, see I.²

$\Delta\nu = 520(4)$ and $535(4).9; 624(3).9; 646(3)$ and $665(4).7; 700(3).9; 902^*(2).6; 968^*(2); 1000(6).3; 1023^*(3)<.7; 1153^*(3)$ and $1181(3).7; 1244(5).9; 1263(6).5; 1424(3).8; 1447(4).7; 1491(4).8; 1603(9).7; 2221(10)$ and $2246(10).6; 2918^*(3b).5; 2959^*(2); 2979^*(2); 3063(6).5.$

The frequency 987, previously reported, was not found in the present study.

9. **4-Phenyl-3-butynol-1** ($C_6H_5C\equiv CCH_2CH_2OH$).—Carbon tetrachloride added; for previous data, see I.²

$\Delta\nu = 386(2).9; 528(3b).9; 936(2)<.7; 980(2)<.9; 1000(7).3; 1162(3).9; 1181(3).6; 1241(5)$ and $1259(5).5; 1432(3)$ and $1440(3).7; 1602(9).8; 2214(4)$ and $2233(10).5; 2943^*(3)$ and $2987^*(3).5; 3063^*(6).6.$

10. **5-Chloro-1-phenylpentyne-1** ($C_6H_5C\equiv CCH_2CH_2CH_2Cl$).—Carbon tetrachloride added; for previous data, see I.²

$\Delta\nu = 373(3)$ and $408(1).7; 521(3).7; 625(3).7; 654(4).7; 693(3).7; 1000(7).2; 1154(3).9; 1177(3).6; 1258(7).5; 1435(4).7; 1489(3).7; 1600(8).7; 2220(10)$ and $2236(10).6; 2837^*(1).8; 2913^*(4).4; 2956(3).7; 3063(6).5.$

11. **1,3-Diphenylpropyne** ($C_6H_5C\equiv CCH_2C_6H_5$).—Synthesized by action of benzyl *p*-toluenesulfonate (2 moles) upon phenylacetylenemagnesium bromide (1 mole)¹⁴; b. p. 135–145° (2–3 mm.) (probably somewhat high due to superheating). Not distilled in column. Previous data, none.

$\Delta\nu = \pm 209(5).8; 279(1b); 327(1b); \pm 379(5); 488(1); 513(1); 528(4)<.9; 602(4)$ and $622(5).9; 712(1b); 757(3)<.6; 797(4).9; 813(3); 840(1); 850(1); 910(1b); 947(1); 981(8).2; 1005(8).1; 1032(4).6; 1156(4).9; 1181(6).6; 1249(8b).5; 1287(1b); 1328(1); 1422(3)$ and $1445(2)<.9; 1493(5).7; 1601(9).7; 2212(8).5; 2238(10).5; 2277(1b); 2317(1); 2435(1); 2558(1); 2817(1); 2883(5)$ and $2898(3).5; 3065(8b).5; [3202(1)].$

12. **1-Phenyl-1-butynol-3** ($C_6H_5C\equiv CCHOHCH_3$).—Synthesized by action of acetaldehyde upon phenylacetyl-

enemagnesium bromide, b. p. 123° (9 mm.); for previous data, see Gredy.¹⁵

$\Delta\nu = 174(4b)$ and $189(4).8; 260(1); 298(1); 349(1); 360(3).9; 433(1); 524(1); 546(4).8; 582(2).9; 621(2).9; 707(1b).9; 756(2).9; 850(1); 935(5).4; 1001(8).3; 1024(1); 1077(1); 1112(2b)<.6; 1158(4).6; 1175(4).6; 1237(1); 1255(7).4; 1276(1); 1323(1); 1385(1); 1445(2).7; 1491(3).7; 1599(9).7; 2198(4).7; 2233(10).6; 2870(2b).5; 2936(3b).4; 2985(2b).7; 3062(5).6.$

Gredy's 463 e is probably 2233 k. 489 e was not observed in the present study. 1485 e may be a misprint for 1445 e.

A graphical presentation of those lines for which definite depolarization factors were obtained is given in Fig. 1. The broad lines in the figure correspond to cases in which two lines were not clearly separated on the polarization film. The depolarization factor, multiplied by 10 in order to simplify the diagram, is written near the line to which it corresponds. The height of the line is proportional to its intensity.

Discussion of Results

The data clearly indicate that in the seven cases where it was possible to distinguish two lines on the polarization film in the 2200 cm^{-1} region, they were both depolarized to the same degree, within experimental error. Since symmetrical vibrations are in general strongly polarized, asymmetrical vibrations strongly depolarized, it is thus impossible to account for the lines observed in the present study by supposing that they correspond one to a symmetrical, the other to an asymmetrical, vibration, as Glockler and Davis⁶ state to be the case for dimethylacetylene.

The two molecular forms proposed by Gredy³ to account for the splitting are $RC\equiv CR'$ and $R'>C^+\equiv C^-$. The presence of any appreciable portion of the latter compound seems to be ruled out, on a purely physical basis, however, by the extremely small dipole moments obtained for many symmetrical disubstituted acetylenes, such as diphenyl-, di-*n*-butyl-, and di-*n*-amylacetylene. Wenzke and Allard¹⁶ conclude that the simplest structure consistent with zero moment is $RC\equiv CR'$ and state that "the presence of an appreciable portion of the acetylidene compound is obviated." Furthermore, the acetylidene form is very difficult to justify on the basis of the facts of organic chemistry.

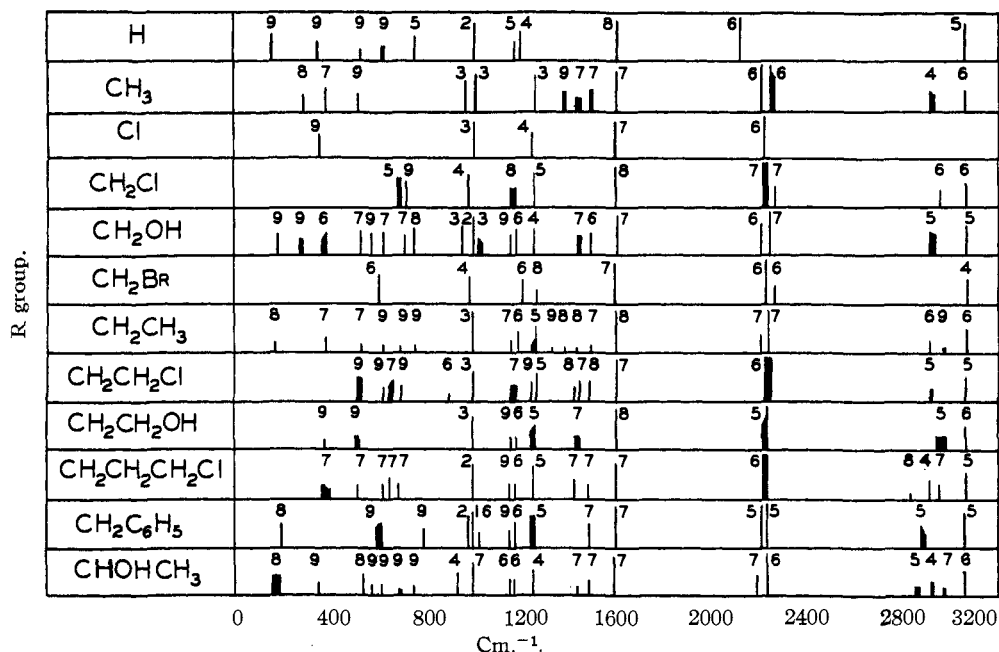
In regard to Badger's suggestion that the split-

(15) B. Gredy, *Ann. chim.*, [11] 4, 5 (1935).

(16) H. H. Wenzke and R. P. Allard, *THIS JOURNAL*, 56, 859 (1934).

(13) 408 e in $C_6H_5C\equiv CCH_2CH_2CH_3$, measured by Gredy, is also probably 2238 k.

(14) J. R. Johnson, A. M. Schwartz and T. L. Jacobs, *THIS JOURNAL*, 60, 1885 (1938).

Fig. 1.—Raman spectra of compounds of the type $C_6H_5C\equiv CR$.

ting is due to a Fermi resonance interaction, it may be noted that there occurs in the present results no frequency whose first overtone would lie in the 2200 cm.^{-1} region. This is in agreement with Badger's prediction that the frequency near 1100 cm.^{-1} would not be active in the Raman effect. There is, however, a frequency at 756 cm.^{-1} whose second overtone falls at approximately the same frequency as the mean of the two lines near 2200 cm.^{-1} . The extent of the agreement for the various compounds is indicated in Table I. It

acetylenes as would need be the case if it is to provide a universal cause for the splitting in acetylenic compounds. The investigation of Badger's hypothesis is being continued by studies in both Raman and infrared absorption spectra.¹⁷

Acknowledgment.—It is a pleasure to acknowledge grants in aid of this research program by the American Association for the Advancement of Science, Sigma Xi, and the Virginia Academy of Science.

Summary

1. Raman frequencies and depolarization factors are reported for twelve acetylenic compounds of the type $C_6H_5C\equiv CR$, where R is H, Cl, CH_3 , C_2H_5 , CH_2OH , CH_2Cl , CH_2Br , CH_2CH_2OH , CH_2CH_2Cl , $CHOHCH_3$, $CH_2C_6H_5$, and $CH_2CH_2CH_2Cl$.

2. The two lines near 2200 cm.^{-1} were found to have the same depolarization factors, thus indicating that one frequency cannot correspond to a symmetrical, the other to an asymmetrical, vibration as Glockler and Davis have stated to be the case for dimethylacetylene.

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RECEIVED SEPTEMBER 25, 1939

R	"Triple bond" frequencies		Mean	Second overtone
CH_3	2214	2254	2234	2274
CH_2Cl	2222	2263	2243	2268
CH_2Br	2226	2265	2246	2271
CH_2OH	2202	2242	2222	2268
CH_2CH_3	2206	2238	2222	2271
CH_2CH_2Cl	2204	2233	2218	2262
$CH_2C_6H_5$	2212	2238	2225	2271
$CHOHCH_3$	2198	2233	2215	2268

will be noticed that the frequency of the overtone is somewhat greater than the mean of the two frequencies in each case and although the 756 cm.^{-1} frequency appears with remarkable constancy in the spectra of derivatives of phenylacetylene, it has not been observed with similar constancy in the spectra of other disubstituted

(17) In a recent paper on the Raman and infrared absorption spectra of dimethylacetylene, Crawford [*J. Chem. Phys.*, **7**, 555-562 (1939)] reports a weak frequency at 1126 cm.^{-1} in the infrared spectrum which he regards as the fundamental whose first overtone interacts with the fundamental near 2270 cm.^{-1} to produce the doublet 2233, 2310 observed in the Raman spectrum. In this case, the frequency of the overtone is less than the mean of the doublet, rather than greater as in the compounds discussed above.