bond order against bond length, and attempts have been made to give these curves a theoretical or semi-theoretical basis. Empirical equations connecting these two internuclear properties have been suggested. It is assumed now, as in the past, that single, double and triple bonds have their conventional orders, and second order refinements are properly neglected.

For the hydrogen molecule, $r_e = 0.74$ Å., $n = 1$, and for the hydrogen molecule ion, $r_e = 1.06$ Å., $n = 0.5$. Also, $(1/r_e^2) = 1.826$ and 0.890, which figures suggest that bond order and $1/r_e^2$ have some connection. This possibility may be tested rigorously for carbon–carbon bonds. The carbon–carbon bond length in ethane is 1.543 Å., in ethylene 1.353 Å., and in acetylene 1.207 Å. Also, using the rotational Raman spectrum, Stoicheff[1] has found that the C–C distance in benzene is 1.397 Å., and by the molecular orbital method; Coulson[2] has evaluated the C–C bond order in this molecule as 1.67. If now bond order is plotted against $1/r_e^2$ an excellent straight line is obtained, having the equation

$$1/r_e^2 = 0.2868 + 0.1334n \tag{1}$$

In Table I, the last column gives values of r_e calculated using equation (I).

TABLE I

n	r_e, Å.	$1/r_e^2$	$(r_e)_c$, Å.
1	1.543	0.4202	1.543
1.67	1.397	0.5121	1.401
2	1.353	0.5462	1.344
3	1.207	0.6868	1.207

For the carbon–nitrogen pair,[3] bond length information is on a lower plane of accuracy. A careful assessment of the data available on the C–N single bond has given the value 1.475 Å., and for the triple bond spectroscopic methods have led to 1.156 Å. Again, theoretical bond orders calculated by the molecular orbital method, and experimental bond lengths are available for the molecules, melamine and pyridine. For melamine, the bond order of each C–N bond is 1.658, and the bond length 1.346 Å., and for pyridine the values are 1.534, and 1.37 Å. Table II gives the data, the equation to the line being;

$$1/r_e^2 = 0.316 + 0.144n \tag{2}$$

TABLE II

n	r_e, Å.	$1/r_e^2$	$(r_e)_c$, Å.
1	1.475	0.460	1.475
1.53	1.37	0.533	1.37
1.66	1.346	0.552	1.35
3	1.156	0.748	1.156

For nitrogen–nitrogen bonds, the single bond distance is known from electron diffraction measurements on hydrazine to be 1.48 Å. The double bond distance in azomethane is 1.24 Å., and the triple bond distance in nitrogen is 1.094 Å. A plot of bond order against $1/r_e^2$ gives an almost perfect straight line having the equation;

$$1/r_e^2 = 0.263 + 0.193n \tag{3}$$

Similar relationships probably exist for carbon–oxygen and carbon–sulfur bonds.

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RECEIVED MAY 9, 1955

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(1) B. P. Stoicheff, *Com. J. Phys.*, **32**, 635 (1954); G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

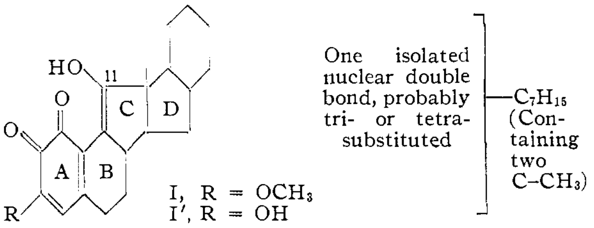
(2) C. A. Coulson, *Proc. Roy. Soc.*, **169A**, 413 (1939).

(3) E. G. Cox and G. A. Jeffrey, *ibid.*, **207A**, 110 (1951).

STRUCTURE OF PRISTIMERIN AND CELASTROL[1]

Sir:

Pristimerin is an antibiotic isolated from *Pristimera indica* and *P. grahami* (*Celastraceae*),[2] which besides being active against the common gram-positive organisms, is characterized by its activity against the *Viridans* group of Streptococci. Comparison of the melting point, ultraviolet and infrared spectra of pristimerin with celastrol monomethyl ether[3] showed that the two compounds were identical.[4] We wish to present structure I for pristimerin and I′ for celastrol as a working hypothesis.



I, R = OCH_3
I′, R = OH

Pristimerin, $C_{30}H_{40}O_4$ (Calcd.: C, 77.55; H, 8.68. Found: C, 77.54; H, 8.87), orange needles, m.p. 219–220°, possesses one methoxyl group and at least three C-methyl groups (Kuhn–Roth: Found 2.5 groups): $\lambda_{\text{infl.}}^{\text{alc.}}$ 250–255 mμ (log ε 3.90), $\lambda_{\text{min.}}^{\text{alc.}}$ 305 mμ (log ε 2.65), $\lambda_{\text{max.}}^{\text{alc.}}$ 423 mμ (log ε 4.05).[5] The reversible nature of color discharge, when reacted upon by reducing agents, *e.g.*, PtO_2–H_2, sodium hydrosulfite, etc., and the similarity in the shape[6] of the ultraviolet spectrum with that of model *o*-quinones, *e.g.*, 3-methoxy-1,2-benzoquinone ($\lambda_{\text{min.}}^{\text{alc.}}$ 290 mμ, log ε 2.68; $\lambda_{\text{max.}}^{\text{alc.}}$ 370 mμ, log ε 3.31) suggested that two of the oxygen functions were contained in an *o*-quinonoid arrangement. However, the colorless reductive acetate II, $C_{34}H_{46}O_6$ (Calcd.: C, 74.15; H, 8.42. Found: C, 73.75; H, 8.29), m.p. 252°, $[\alpha]^{22}\text{D}$ +54.3 ($CHCl_3$), did not show any conspicuous maxima in the ultraviolet, excepting a shoulder-like peak at 278 mμ (log ε 2.90), which at most could only be attributed

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(1) The present studies were commenced in the laboratory of Professor L. F. Fieser, Harvard University.

(2) S. S. Bhatnagar and P. V. Divekar, *J. Sci. Industr. Res.*, **10B**, 56 (1951).

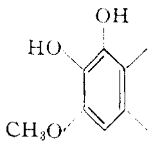
(3) O. Gisvold, *J. Am. Pharm. Soc.*, **28**, 449 (1939); **29**, 12 (1940); **31**, 529 (1942); L. F. Fieser and R. N. Jones, *ibid.*, **31**, 315 (1942); M. S. Schechter and H. L. Haller, THIS JOURNAL, **64**, 182 (1942).

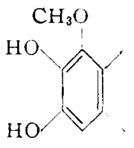
(4) We are indebted to Professor O. Gisvold, University of Minnesota, for kindly furnishing us a sample of celastrol and the monomethyl ether. The probable identity of pristimerin and celastrol methyl ether has been previously noted by Kulkarni and Shah[11] and by Kamat, *et al.*[14]

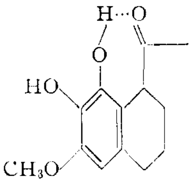
(5) Though the infrared spectrum has been compared with those of several other *o*-quinones, we have not been able to make satisfactory assignments in the 6 μ region: $\lambda_{\text{max.}}^{\text{Nujol}}$ 3350 w, 1742 s, 1736 s, 1662 m, 1595 s, 1550 m, 1519 m; $\lambda_{\text{max.}}^{CCl_4}$ 3380 w, 1740 s, 1655 w, 1607 s, 1514 m.

(6) The batho- and hyper-chromic shifts encountered in the spectrum of pristimerin in comparison to other *o*-quinones is now attributed to the conjugated double bond.

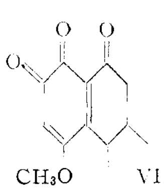
to a benzenoid ring; $\lambda_{\text{max.}}^{\text{CHCl}_3}$ 1775 and 1765 (phenol acetate), 1725 (carbonyl), 1600 and 1515 cm.$^{-1}$ (aromatic), no band in 3 μ (hydroxyl) region. A zinc-dust distillation of 600 mg. of I afforded 3 mg. of strongly fluorescent III, $C_{26}H_{22}$ (Calcd.: C, 93.40; H, 6.60. Found: C, 93.43; H, 6.87), dec. 299–300° (in sealed tube; otherwise sublimation occurred); the ultraviolet spectrum was superimposable on that of picene except that the peaks, totalling eleven, were located 0–2 mμ toward longer wave length. Hence III is regarded as a picene monosubstituted with a C_4H_9 side-chain.[7] Although possibility of ring formation during the procedure must not be overlooked, a pentacyclic skeleton has tentatively been assumed since evidence cited later suggested the existence of rings A, B, and C; the five-membered nature of ring C is discussed below. One mole of hydrogen was absorbed upon reduction of I with Adams catalyst in acetic acid to give pristimerol IV, $C_{30}H_{42}O_4$ (Calcd.: C, 77.21; H, 9.07. Found: C, 77.12; H, 9.02), m.p. 241°, $\lambda_{\text{max.}}^{\text{alc.}}$ 284 mμ (log ϵ 3.49), $\lambda_{\text{max.}}^{\text{Nujol}}$ 3580, 3350, *1705* (carbonyl), 1625, 1610, and 1515 cm.$^{-1}$. IV is obtained in better yield from the reaction of sodium borohydride on I; IV-di-*p*-nitrobenzoate, $C_{44}H_{48}O_{10}N_2$ (Calcd.: C, 69.09; H, 6.33; N, 3.66. Found: C, 69.02; H, 6.65; N, 3.72), m.p. 213°. Action of dimethyl sulfate on IV afforded pristimerol dimethyl ether V, $C_{32}H_{46}O_4$ (Calcd.: C, 77.69; H, 9.37. Found: C, 77.77; H, 9.54), m.p. 215°, $\lambda_{\text{max.}}^{\text{alc.}}$ 280 mμ (log ϵ 3.31), $\lambda_{\text{max.}}^{\text{Nujol}}$ *1720* cm.$^{-1}$ (carbonyl). Comparison of the ultraviolet spectrum of V with various hydroxy- and/or methoxy-benzenes indicated a 1,2-dialkyl-3,4,5-trimethoxy benzene moiety to be present. Accordingly, 1,2,3,4-tetrahydro-5,6,7-trimethoxynaphthalene[8] was synthesized and the spectrum was found to be superimposable on that of V: $\lambda_{\text{max.}}^{\text{alc.}}$ 281 mμ (log ϵ 3.30). Hence IV possesses the partial structure (a) or (b), and I possesses the corresponding quinonoid structure; apparently this may only be incorporated in a terminal skeletal ring. The *o*-quinonoid group of I is hindered, as evidenced from the unreactivity with *o*-phenylenediamine; the carbonyl group apparent in the infrared spectra of II, IV, and V was also unreactive and afforded no carbonyl derivatives. These facts may be satisfied by assuming a rather rigid structure for these functions, *i.e.*, by adopting (a) for IV and placing the ketone group in the sterically hindered position as in VI. The bathochromic shift of the ketone band in the infrared spectrum of IV as compared with II and V is explicable in terms of a hydrogen bridge. Assignment of a five rather than a six-membered ring to ring C is based on the infrared absorption: the 11-keto in the five-membered ring C of hydrojervine derivatives absorb in the region 1725 cm.$^{-1}$.[9] However, possibilities for a six-membered C-ring still remains as an alternative. An angular methyl group has been placed at the ring C/D junction to account for the formation of a picene. The 11-oxygen function in I has been formulated in the enol-form rather than in the keto-form to explain the consistent appearance of an infrared band at 3350–3400 cm.$^{-1}$ (solution and *solid;* also no shift upon changing concentration of solution),[10] and the presence of one set of isosbestic points in the ultraviolet spectra measured in alcoholic alkali (362 mμ, ϵ = 4800; 495 mμ, ϵ = 3300). The fact that ozonolysis of I afforded no volatile products, and that only one mole of hydrogen was absorbed upon catalytic hydrogenation suggested the absence of side-chain double bonds and unhindered double bonds.

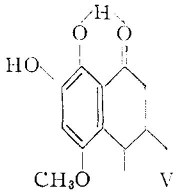

(a)


(b)


VI

Kulkarni and Shah[11] have assigned to I the partial structure VII; pristimerol would then be represented by the conjugate-chelated VIII. The latter should now show the characteristic infrared[12] and ultraviolet[13] absorption of *o*-hydroxyacetophenones, both of which are against facts. The fact that celastrol and celastrol methyl ether (hence pristimerin) possess similar ultraviolet absorption curves[3] and that the latter is derived from the former by diazomethane is also inconsistent with this expression, *i.e.*, a demethylated VII (celastrol) would be methylated to give a *p*-quinone. Recently, Kamat, *et al.*,[14] have proposed for pristimerin a structure composed of a diosphenol and a conjugated pentaene moiety. This can also be excluded on grounds of ultraviolet absorption since the chromorphoric power of both groups are insufficient to produce absorption at 423 mμ.[15] We intend to publish details of the present work in *Bull. Chem. Soc. Japan.*


VII


VIII

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[7] With di-alkyl-substituted picenes, *e.g.*, 1,8-dimethylpicene, a bathochromic shift of 5-7 mμ is observed (L. Ruzicka and E. Mögell, *Helv. Chim. Acta*, **19**, 377 (1936)). The spectrum was also comparable with that of chrysene and analysis equally agreed with a C_3H_7-substituted chrysene, $C_{21}H_{18}$ (Calcd.: C, 93.29; H, 6.71). However, the observed bathochromic shifts of 6–17 mμ of the respective peaks are too high to be regarded as being produced by three methyl groups.

[8] R. D. Haworth, B. P. Moore, and P. L. Pauson, *J. Chem. Soc.*, 3271 (1949).

[9] O. Wintersteiner, M. Moore, and B. M. Iselin, THIS JOURNAL, **76**, 5609 (1954).

[10] This is contrary to the statement of Kulkarni and Shah[11] that no hydroxyl band is present. Samples used for present measurements were carefully recrystallized from absolute solvents and thuroughly dried.

[11] A. B. S. Kulkarni and R. C. Shah, *Nature*, **173**, 1237 (1954).

[12] H. L. Hegert and E. F. Kurth, THIS JOURNAL, **75**, 1622 (1953).

[13] R. A. Morton and A. L. Stuffs, *J. Chem. Soc.*, 1347 (1940).

[14] V. N. Kamat, F. Fernandes, and S. S. Bhatnagar, *J. Sci. Industr. Res.*, **14C**, 1 (1955).

[15] W. Oroshnik, A. D. Mebane, THIS JOURNAL, **76**, 5719 (1954).

Acknowledgment.—The authors are greatly indebted to Col. S. S. Bhatnagar, St. Xavier's College, Bombay, for generously supplying us the material used in the present studies, and to Professor L. F. Fieser, Harvard University, for permitting us to publish the results obtained while one of us (K. N.) was working in his laboratory on pristimerin.

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RECEIVED APRIL 26, 1955

BOOK REVIEWS

Bibliography of Ozone Technology. Volume 1. Analytical Procedures and Patent Index. By CLARK E. THORP, Manager, Department of Chemistry and Chemical Engineering, Armour Research Foundation of Illinois Institute of Technology, Technology Center, Chicago 16, Illinois. Armour Research Foundation, 10 West 35th Street, Chicago 16, Illinois. 1954. 209 pp. 14.5 × 22.5 cm. Price, $5.25.

This book is the first of a proposed series dealing with the chemistry of ozone. The stated object of the author is to make available to others the large bibliography in the rapidly expanding field of ozone chemistry which he and his associates have accumulated. The first part of the volume lists two hundred and sixty-six references dealing with analytical methods for gaseous ozone. Following most of these is a brief statement indicating the sort of information to be found in the reference. Factual information is sometimes given but generally no systematic attempt has been made to abstract the articles. Likewise no critical evaluations are included. The list goes back over one hundred years and the author has striven to include some reference to all published methods of ozone analysis regardless of its vintage.

Part two lists, without comment, nine hundred and eighty patents related to ozone. These are separated into fifty-two groups, such as Air Conditioning, Generators, Ozone-resistant Materials, and the like. The author believes that the list up to 1954 is at least 90% complete but warns the reader that other pertinent patents may exist under obscure classifications. The volume index is categorized according to Author, Subject, Patentee and Patent Number. This publication should prove to be highly useful to everyone who is concerned with research involving ozone.

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Glutathione. Proceedings of the Symposium Held at Ridgefield, Connecticut, November, 1953. By S. COLOWICK, A. LAZAROW, E. RACKER, D. R. SCHWARZ, E. STADTMAN and H. WAELSCH (Editors). Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1954. x + 341 pp. 16 × 23.5 cm. Price, $7.50.

This book is a collection of 29 papers which were presented at the symposium. As a very worthwhile feature, the book also includes transcripts of discussions of the papers at the symposium. All angles of the subject of Glutathione are covered: Properties and Organic Chemistry, The Methods for Detection and Assay of Glutathione and Sulfhydryl Compounds, Biochemical Mechanisms, and Physiological Action and Clinical Aspects. Approximately 1000 literature citations are included. With nearly 60 contributors, the quality and clarity of presentation of the material is not uniform, but the over-all impression is one of excellence.

The editors and publishers are to be commended for the inclusion of excellent indices and for the fine workmanship which went into preparation of the book. Few typographical errors were noted, and with the exception of two transposed figures (p. 63 and 68) the errors cause no confusion.

This book will be invaluable for anyone interested in glutathione, whether he is actively working in the field or merely needs a bit of information for use in some other field.

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Einführung in die Ultrarotspektroskopie. By WERNER BRÜGEL, Physiker in der Badischen Anilin- and Soda-Fabrik AG., Ludwigshafen a. Rh. Dietrich Steinkopff Verlag, 16, Darmstadt, Holzhof-Allee 35, Germany. 1954. xii + 366 pp. 15.5 × 22 cm. Price, Brosch, DM 46.-, Geb. DM, 49.-.

Before 1940 infrared spectroscopy was a specialty practiced by a few devotees on instruments designed and constructed in their own laboratories. It has since expanded so enormously that there are probably in the neighborhood of 2000 infrared spectrometers in use today, and it has become an important adjunct to research in all branches of chemistry as well as a useful analytical tool for both the laboratory and the factory. Nevertheless, since the excellent early work by Schaeffer and Matossi, no adequate introduction to the theory and practice of the field which takes into account the newer developments has been published. Dr. Brügel has attempted to fill the need for such an introduction, primarily directed to the "practical" spectroscopist, and whereas this reviewer does not always agree with the author as regards the selection and balance of material his work is, by and large, successful.

The first quarter of the book is devoted to the theory of rotational spectra, rotation-vibration spectra, molecular vibrations and their symmetry properties. As the author acknowledges, this section follows Professor Herzberg's book very closely and has little relation to the remainder of this volume. A discussion of molecular vibrations in terms which might be applicable to the consideration of the spectra of larger molecules is not given at all while much space is devoted to the consideration of fine structure in gas spectra.

The next fifty pages cover light sources, prism monochromator design and calibration, infrared detectors, and general considerations regarding various types of infrared spectrometers and their use. It is curious that the diffraction grating is dismissed in a paragraph as important only for fine structure studies and not for "practical" spectroscopy. In a later section the author stresses the need for the development of techniques to make possible a quantitative "intensity" spectroscopy to parallel the well developed "frequency" spectroscopy; since one obstacle to achieving this goal is inadequate resolution it seems likely that the grating instrument will take its place in the analytical laboratory before long.

Another thirty-five pages are devoted to a description of most of the commercial instruments and accessories produced in Germany, Britain and America. This is followed