borohydride reduction to 1,1-diphenyl-1-methylamino-2-propanol (m.p. 76–76.5°), with periodate cleavage to give benzophenone and acetaldehyde, both isolated as their respective 2,4-dinitrophenylhydrazone derivatives.

All new compounds reported above had acceptable carbon, hydrogen and nitrogen analyses.

CALVIN L. STEVENS
ROBERT D. ELLIOTT
BRADLEY L. WINCH
IRWIN L. KLUNDT
CHEMISTRY DEPARTMENT
WAYNE STATE UNIVERSITY
DETROIT 2, MICHIGAN

RECEIVED APRIL 25, 1962

Fe^{57} MÖSSBAUER RESONANCE AND COMPARISON OF BONDING IN $C_8H_8Fe_2(CO)_6$ AND $C_8H_8Fe(CO)_3$

Sir:

Since the initial[1] reported isolation of the compound (COT)[$Fe(CO)_3$]$_2$ (COT = cycloöctatetraene), a number of speculations regarding the structure of this compound[2] and its relationship to the compound (COT)$Fe(CO)_3$ have been published. As Cotton has pointed out,[3] all of the proposed structures ranging from nearly planar rings to the well-known tub form will give nearly identical nuclear magnetic resonance spectra. Manuel and Stone[2] have examined the infrared spectra of COT-[$Fe(CO)_3$]$_2$ in $CHCl_3$ and CS_2 and have considered both the planar and the tub configuration of the COT ring as possible structures. As pointed out by them (as well as by Cotton[3], but only for the binuclear compound) the definitive data with respect to the structure of these compounds must be sought in X-ray scattering studies.

Such investigations have been carried out by Lipscomb and Dickens both on (COT)$Fe(CO)_3$[4] and (COT)[$Fe(CO)_3$]$_2$,[5] and the pertinent parameters are summarized in the first three lines of Table I.

TABLE I

COMPARISON OF STRUCTURAL PARAMETERS[4,5] AND RESONANT GAMMA ABSORPTION PARAMETERS FOR (COT)$Fe(CO)_3$ AND (COT)[$Fe(CO)_3$]$_2$

	(COT)$Fe(CO)_3$	(COT)($Fe(CO)_3$)$_2$
Fe–C_{end}[a]	2.05	2.06
Fe–C_{centr}[a]	2.18	2.15
Fe–C≡[a]	1.80	1.78
ΔE[b]	1.23	1.32
δE[b]	0.23	0.18
$\Gamma_{1/2}$[b]	0.32	0.33

[a] Values in A. ±0.3. [b] Values in mm. $sec.^{-1}$ ±0.01 at 78°K.

We have used both of these compounds as thin absorbers in a Mössbauer resonance experiment[6,7] using Co^{57} diffused into metallic chromium as a source. The results of these measurements are summarized in the last three lines of Table I, in which ΔE is the quadrupole splitting, δE is the isomer shift[8,9] and $\Gamma_{1/2}$ is the full width at half height of the resonance line. Both compounds show essentially no resonant absorption at room temperature. At liquid nitrogen temperature, on the other hand, the resonance effect of a 0.25 mm. thick absorber is on the order of 15 to 20% and thus easily measurable with considerable precision. The velocity scale was calibrated using a value of 3.95 mm. $sec.^{-1}$ for the ground state splitting of Fe^{57} in soft iron.[10]

The near identity of the two sets of values for ΔE, δE and $\Gamma_{1/2}$ for the two compounds leaves little doubt concerning the close similarity of the environment of the iron atoms in these substances. Clearly the near planarity of the C_4 residue in the mono-iron compound[3,4] is essentially preserved in the bis-iron compound, and a structure such as IV of ref. 3 can be ruled out. While the difference in the Fe–C bond distances reported[4,5] for the two compounds is within the quoted experimental error of ±0.02Å., the larger quadrupole splitting in (COT)[$Fe(CO)_3$]$_2$, which arises from the interaction between the electric field gradient at the iron nucleus and the nuclear quadrupole moment of the 14.4 Kev. level in Fe^{57}, is consistent with the shorter Fe–$C_{centr.}$ and Fe–C (carbonyl) distance in the hexacarbonyl compound. That the quadrupole splitting observed for these compounds is sensitive to the molecular structure and bonding—in the present case specifically to charge delocalization—is clearly indicated by the fact that the ΔE values reported in Table I are appreciably different from those which we have measured for related compounds, *e.g.*, $(COT)_2Fe(CO)_3$ (1.60 mm. $sec.^{-1}$),[11] and (COT)[$C_2(CN)_4$)] $FeCO_3$ (0.86 mm. $sec.^{-1}$)[11].

Moreover, the near identity of the parameter $\Gamma_{1/2}$ for the two compounds precludes any appreciable difference in the environments of the two iron atoms in (COT)[$Fe(CO)_3$]$_2$, since such a difference would be observed as line broadening of one of the two peaks of the quadrupole split pair with respect to the other (which is not observed), or with respect to $\Gamma_{1/2}$ for (COT)$Fe(CO)_3$. Although much of the line broadening arises from effects in the source, it is worthwhile noting that $\Gamma_{1/2}$ = 0.33 ± 0.01 mm. $sec.^{-1}$ is essentially identical with the value we have observed[12] for $Fe(CO)_5$ and $(COT)_2Fe(CO)_3$ at 78°K., but substantially smaller than the line width observed for other iron carbonyl compounds[13] which do not contain the (COT) ring, at the same temperature.

Finally, it may be noted that the very small isomer shifts in Table I are consistent with the values

---

[1] T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 60 (1959); M. Rausch and G. N. Schrauzer, *Chem. and Ind.*, 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959); G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

[2] T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960); D. A. Brown, *J. Inorg. Nuclear Chem.*, **10**, 39 (1959); **10**, 49 (1959).

[3] F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

[4] B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

[5] B. Dickens and W. N. Lipscomb, *ibid.*, **83**, 489 (1961).

[6] R. L. Mössbauer, *Z. Physik*, **151**, 124 (1958).

[7] For a review of this technique, see "The Mössbauer Effect," H. Fraunfelder, W. A. Benjamin Co., New York, N. Y., 1962.

[8] O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960); S. De Benedetti, G. Lang, and R. Ingalls, *ibid.*, **6**, 60 (1961).

[9] L. R. Walker, G. K. Wertheim and V. Jaccarino, *ibid.*, **6**, 98 (1961).

[10] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston and D. H. Vincent, *Phys. Rev. Letters*, **4**, 28 (1960).

[11] G. K. Wertheim and R. H. Herber (to be published). We are indebted to Dr. G. N. Schrauzer for generous samples of these compounds.

[12] G. K. Wertheim and R. H. Herber, to be published.

[13] R. H. Herber, W. Robinson and G. K. Wertheim, *J. Chem. Phys.*, in press.

which have been observed[14] for other zero oxidation state iron compounds. These data suggest[9] essentially completely covalent bonding between the iron atom and the π electron distribution in the (COT) ring. Available n.m.r. and kinetic data for $C_8H_8Fe(CO)_3$ suggest that bonding to the $Fe(CO)_3$ group leads to strong electron delocalization in the ring. This delocalization is implied in the π-π overlap integral calculations given by Dickens and Lipscomb[4,5]. The present results indicate that the charge density of the delocalized π electrons is essentially the same in the C_4 residue of $C_8H_8Fe(CO)_4$ as in the two C_4 residues in $C_8H_8Fe_2(CO)_6$ to which the iron atoms are bonded. This model is consistent with the *quasi*-octahedral configuration of the iron atom with respect to three CO groups and three of the eight carbon–carbon bonds suggested by Dickens and Lipscomb.[4]

A more detailed study of resonant gamma ray absorption studies in iron carbonyl compounds will be published elsewhere. We are greatly indebted to Prof. F. G. A. Stone and Dr. G. N. Schrauzer for generously supplying samples of these compounds and to D. N. E. Buchanan and Miss W. Robinson for assistance with the measurements. This work was supported in part by the U. S. Atomic Energy Commission.

BELL TELEPHONE LABORATORIES G. K. WERTHEIM
MURRAY HILL, NEW JERSEY, AND
NUCLEAR SCIENCE CENTER
RUTGERS UNIVERSITY R. H. HERBER
NEW BRUNSWICK, NEW JERSEY

RECEIVED MARCH 28, 1962

---

(14) L. M. Epstein, *J. Chem. Phys.*, in press, private communication.

BOOK REVIEWS

The Parathyroids. Proceedings of a Symposium on Advances in Parathyroid Research, held at the Rice Institute, now Rice University, Houston, Texas. Edited by ROY O. GREEP, Ph.D., Professor of Anatomy and Dean, Harvard School of Dental Medicine, and ROY V. TALMAGE, Ph.D., Professor of Biology and Chairman of the Department, Rice University. Charles C. Thomas, Publishers, 301–327 East Lawrence Avenue, Springfield, Illinois. 1961. xvii + 473 pp. 18 × 25.5 cm. Price, $12.25.

As is apparent from the sub-title, this volume records the proceedings of a symposium on recent advances in parathyroid research held in February, 1960. The occasion was noteworthy in several respects and will be long remembered by the participants (including this reviewer) as a landmark in the field. First, the invited speakers were distinguished for their imaginative morphological, biochemical or physiological investigations of the parathyroid glands and their secretions. In addition, many of the men who pioneered the investigation of parathyroid physiology were present to comment on the new work which was presented. A unique feature of the program were several short formal tributes to these men in which the importance of their contributions as a basis for current studies was made clear for the younger workers present. Second, although the group was large—over 200 attended—extensive and spirited discussion followed the formal presentations in each session. The excellent physical arrangements made possible the recording of these comments which are included almost verbatim in the book.

The third and most noteworthy aspect of this symposium was that, in a sense, it underlined the emergence of a new era of parathyroid research. Several aspects contributed to this. For the first time the hormone itself seemed to be available in pure form in sufficient quantity to be characterized in terms of its chemical structure as well as its physiological effects. In addition, the first reports of the results of concerted efforts to examine *in vitro* the over-all metabolic patterns of bone cells at the biochemical level and the effects of hormones on these patterns were given. Perhaps most important, however, was that it was abundantly apparent that the two rather rigid "schools"—one believing the primary site of action of the hormone was kidney, the other bone—which had guided thinking in this field were replaced by a general acceptance of multiple sites of action for the hormone. Action at each of these sites, it appeared to be agreed, was such as to lead to an elevation of the serum calcium ion concentration. Thus the way seemed to be opened to examine the mode of action of the pure hormone at the cellular level in several organs and perhaps arrive at a better understanding of the mechanisms involved in controlling the calcium concentration of the blood.

Much of the excitement of the occasion is reflected in this publication of the proceedings both through the papers themselves and the records of the discussion which followed them. The editors have arranged these in six sections which follow, but not completely, the order of the symposium program. While the changes in order of presentation add to the development of the subjects discussed in the formal papers, they tend to detract from the value of the discussion. In these comments reference is made in several places to work already presented in the symposium but which appears later in the book. This also leads to some confusion of the reader perusing McLean's introduction to the body of the symposium in which he summarized the unsolved problems in parathyroid research and explained the program.

The first section entitled "Keynotes in Parathyroid Research" includes besides McLean's excellent introduction and summation, a description by Gaillard of his classic observations of the effects of parathyroid hormone on the histology of bone in tissue culture. Each of these is preceded by the introduction of the speaker by an old friend—a touch which adds warmth and human interest to the book. This section is followed by sections dealing with the cytology of the gland and the chemistry of the hormone, certain selected topics in parathyroid physiology, the relationship of the parathyroids to bone, to citric acid, and to the kidney, and finally a group of papers on parathyroid dysfunction in man. In each the formal papers outline the problems in need of solution, the current state of thinking in the particular area under discussion, and present many previously unpublished observations. In addition, several new working hypotheses concerning the mechanisms by which parathyroid hormone exerts its actions are proposed. Disagreement was not uncommon and this, together with the degree to which these presentations stimulated the participants, is well brought out in the published discussion. These comments include, as well, new and often highly intriguing observations pertinent to the topic under consideration. A unique feature is the inclusion at the end of several of the sections of the formal tribute to the man whose pioneering work was especially concerned with the area under discussion.

Here is a book, then, which includes in a single volume a description of the means of isolation and major chemical features of parathyroid hormone and indicates through selected papers and discussion by workers actively engaged in the field the present status of investigation of its physiological action together with the directions being taken in further studies of unsolved problems. The inclusion of discussion and the tributes, formal and informal, add to the readability and interest of the book as well as reviewing for the newcomer some of the background of the work and the