thoroughly washed with methylene chloride. The filtrate and washing were combined and evaporated to leave a colorless, crystalline mixture of two products (TLC). These were separated by column chromatography on 100 g of silica gel using methylene chloride as eluent. The 6H isomer **17**, 1.3 g (30%), was eluted first and then the more polar 4H isomer **3**, 1.2 g (28%), was obtained. A sample of compound **3** was vacuum sublimed at 140°, giving colorless crystals: mp 168–169°; ir (Nujol) 1620 and 1575 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 4.75 (s, 2 H) and 7.3–8.2 (m, 9 H); mass spectrum *m/e* 231, 265 (100%), and 294 ($M^+$).

Anal. Calcd for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.76; N, 19.00; Cl, 12.03. Found: C, 65.24; H, 3.82; N, 19.14; Cl, 12.09.

A sample of compound **17** was recrystallized from methylene chloride–ether to give colorless crystals: mp 123–125°; ir (Nujol) 1640 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 5.33 (broad s, 1 H), 6.83 (d, 1 H), 7.3–7.7 (m, 6 H), 7.90 (d, 1 H), 8.10 (s, 1 H), and 8.67 (broad s, 1 H); mass spectrum *m/e* 204, 238, 266, and 294 (100%, $M^+$).

Anal. Found: C, 65.49; H, 3.67; N, 19.22; Cl, 11.93.

**8-Chloro-3-methyl-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (4) and 8-Chloro-3-methyl-6-phenyl-6*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (18).** The $MnO_2$ oxidation of amine **14** (3.6 g) under the conditions described above for amine **16** required 48 hr at reflux. The crude mixture of two products (3.0 g) was separated by chromatography on 15 preparative layer plates (silica gel with 5% $CH_3OH$ in $CHCl_3$) giving 1.50 g (42%) of compound **4**, the more polar component, and 0.80 g (22%) of **18**.

A sample of compound **4** was recrystallized from methylene chloride–ether to give colorless crystals: mp 196–196.5°; ir (Nujol) 1620 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.42 (s, 3 H), 4.66 (s, 2 H), and 7.2–8.2 (m, 8 H); mass spectrum *m/e* 245, 279 (100%), and 308 ($M^+$).

Anal. Calcd for $C_{17}H_{13}ClN_4$: C, 66.13; H, 4.24; N, 18.15; Cl, 11.48. Found: C, 66.29; H, 4.46; N, 18.16; Cl, 11.36.

A sample of compound **18** recrystallized from ether had mp 133–135°; ir (Nujol) 1635 and 1555 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.53 (s, 3 H), 5.30 (d, $J$ = 2 Hz, 1 H), 6.8–8.0 (m, 8 H), and 8.48 (d, $J$ = 2 Hz, 1 H); mass spectrum *m/e* 203, 218, 252, 280 (100%), and 308 ($M^+$).

Anal. Found: C, 66.24; H, 4.22; N, 18.44; Cl, 11.81.

**Registry No.**—**3**, 53878-78-7; **4**, 53993-42-3; **5**, 53878-93-6; **6**, 53993-43-4; **7**, 53993-44-5; **8**, 53878-98-1; *syn*-**9**, 53993-45-6; *anti*-**9**, 53993-46-7; **10**, 53879-01-9; **11**, 53993-47-8; **12**, 53993-48-9; **13**, 53993-49-0; **14**, 53993-50-3; **15**, 53879-03-1; **16**, 53879-04-2; **17**, 53879-05-3; **18**, 53993-51-4; 2-amino-5-chlorobenzophenone, 719-59-5; methyl propiolate, 922-67-8; dimethyl acetylenedicarboxylate, 762-42-5; hydroxylamine hydrochloride, 5470-11-1.

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# Nuclear Magnetic Resonance Studies on Conformations about the Nitrogen–Carbon Bond in Some *N*-Malonylimides and Some Comments on the Origin of Nitrogen–Nitrogen Bond Torsional Barriers


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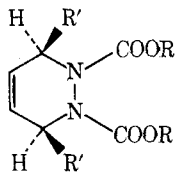
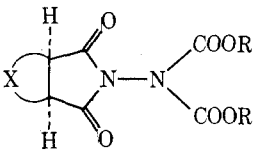
The preparation and NMR studies of a series of *N*-malonyl derivatives of Diels–Alder adducts of anthracene–maleimide and anthracene–citraconimide have been described. In contrast to the tetraacylhydrazine systems, these compounds show no spectral multiplicities in their NMR signals at 44.5° owing to slow rate processes indicating that rotation about the N–C bond in these compounds is free on the NMR time scale. It has been further demonstrated that the nonbonding repulsion between the substituents is not the main contribution to the N–N bond torsional barriers in tetraacylhydrazine systems but that the lone-pair electronic interactions at the two nitrogen atoms are sufficiently effective. This is supported by preparing the sodium salts of the title compounds possessing a >N–$^-$C< system, isoeletronic with the N–N bond in tetraacylhydrazines which show multiplicity in their NMR spectra indicating hindered rotation about the N–C bond.


Studies on conformations by NMR spectroscopy have been receiving considerable attention during recent years.[1] Barriers to nitrogen inversion in cyclic hydrazines[2] and acyclic hydrazines[3] have been studied by dynamic NMR spectroscopy. Hindered inversion at the pyramidal nitrogen in aziridines has been rationalized[4] in terms of ring strain during inversion, while restricted rotation about the N–CO bonds has been assigned[5] to the partial double bond character of the amide bonds. High energy barriers to the inversion of *N,N'*-diacyltetrahydropyridazine of the type I (18–19 kcal/mol)[6] and the restricted rotation about the N–N bonds in tetraacylhydrazine systems of the type II and III[7] have been demonstrated by NMR spectroscopy and attributed largely to the nonbonding repulsions between the acyl substituents in the planar transition state. Existence of nonplanar conformations and high energy barriers to the N–N bond torsion in the *N,N'*-diacyl-*N,N'*-dialkylhydrazine system[8] (21–22 kcal/mol, the values fairly



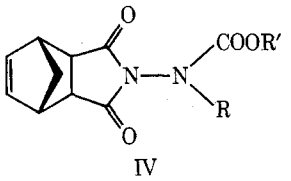
I



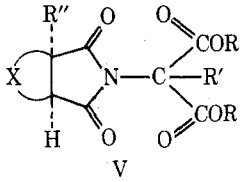
II, X = $-CH_2CH{=}CHCH_2-$

III, X = 9,10-dihydroanthracene

comparable to those of the tetraacylhydrazine system) prompt us to suspect that the nonbonding repulsive interactions between the acyl substituents may not be solely responsible for the high torsional barriers in all these cases. Conformational studies on N′ derivatives of *N*-aminoimides of the type IV,[9] which showed a similar order of barriers (21 kcal/mol) to the N–N bond torsion for the different substituents, R = $CH_3$, $C_6H_5$, COR′, $SO_2R'$, etc., also support the above suggestion. It is on this point that we wish to address this communication along with the NMR studies on the N–C bond system, V, which throw light on the origin of N–N bond torsional barriers.



IV



V

X represents a chain of four or more carbon atoms forming a planar or nonplanar bicyclic cage type structure

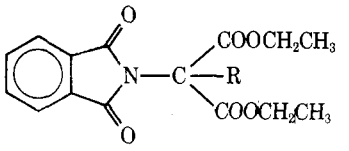
R = $CH_3$, $CH_2CH_3$

R′ = H, $CH_2C_6H_5$, $CH_2CH_3$

R″ = H, $CH_3$

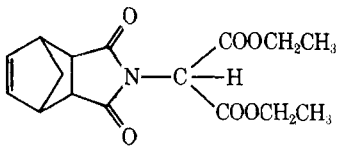
## Results and Discussion

A series of compounds of type V (1–13) has been synthesized and their NMR spectra studied.



1, R = H

2, R = $CH_2C_6H_5$



3

The NMR spectra of compounds 1 and 3 are quite normal. The ester methylene (4 H) and methyl protons (6 H) appear as a sharp quartet (δ 4.3) and a sharp triplet (δ 1.31), respectively, in $CDCl_3$ at 44.5°.

Analogous to the tetraacylhydrazine systems,[10] these compounds may be expected to exhibit slow rotation about the N–C bond and ground-state conformations in which the ester groups would lie one on either side of the imide ring plane. However, neither of these two compounds indicate, from their NMR spectra, any such conformation, stable on the NMR time scale. Even if the N–C bond rotation is slow on the NMR time scale, compound 1, as its imidyl moiety is planar, cannot show any spectral multiplicity, while it may be presumed that the cage moiety of compound 3 is not sufficiently effective to resolve the signals of the two ester groups.

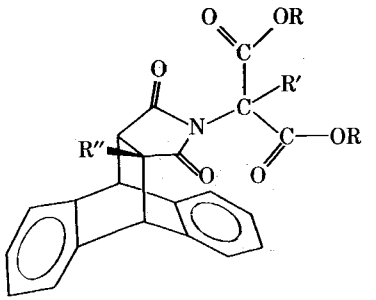
The NMR spectrum of compound 4 in $CDCl_3$ shows (Table I) a singlet for the two ester methyl groups, while that of compound 5 shows (Table I) a normal quartet and a triplet ($J$ = 7.5 Hz) for the two ester ethyl groups. The N compound III (R = $CH_3$) exhibited,[11] in its NMR spectrum, two signals for the two ester methyl groups with an internal chemical shift of 30 Hz, where restricted rotation and nonplanar ground-state conformation about the N–N bond have been inferred. Similarly, if there is any hindrance to the rotation about the N–C bond in compound 4, two different signals for the two ester groups, with an appreciable internal chemical shift, might have been observed. Therefore, it may be presumed that the rotation about the N–C bonds in these compounds is free on the NMR time scale. This has been further verified by the absence of exchange broadening in the signals of compound 4 in $CDCl_3$ at −48°. The NMR spectrum of compound 5 is also consistent with a free rotation about the N–C bond. The ester methylene and methyl group protons in compound 5 resonate at relatively higher fields (δ 4.2 and 1.22, respectively) as compared to the corresponding resonance positions of compounds 1 and 3. This observation indicates that both the ester groups in compound 5 experience a time-averaged shielding effect from the cage moiety, which is an added evidence for the free rotation about the N–C bond.

The spectrum of compound 6 exhibits (Table I) two singlets for the two ester methyl groups, with an internal chemical shift ($\Delta\nu$) of 2 Hz, while that of compound 7 shows (Table I) two quartets ($\Delta\nu$ = 2 Hz) for the ester methylene protons and a broad triplet for the ester methyl protons. The observed multiplicity in signals of the geminal protons of ester groups at the exocyclic carbon atom with a small internal chemical shift may be attributed to the long-range induced asymmetry[12] of the cage moiety due to the $C_{11}$ methyl group.

The NMR spectrum of compound 8 is quite normal (Table I), whereas compound 9 shows a complex multiplet for the four ester methylene protons, a triplet ($J$ = 7.5 Hz) for the six ester methyl protons, and a singlet for the two benzylic protons. The carbon carrying the ester groups in all these compounds is asymmetric when viewed from either of the ester groups.[13] In compound 9, the intrinsic nonequivalence of the two geminal methylene protons of the ester groups caused by so-called asymmetry gives rise to a complex multiplet, while the other signals remain normal. Compound 2 in $CDCl_3$ (as well as in nitrobenzene) also shows a more or less similar pattern, with less resolution, for the ester methylene protons at δ 4.4 (4 H), while it shows normal signals for the rest of the protons: δ 1.29 t (6 methyl protons), 3.88 s (2 benzylic protons) and 7.58 (9 aromatic protons). In compounds 1, 3, 5, and 7, which do not possess a benzyl group at the exocyclic carbon atom, the intrinsic nonequivalence offered by the system is not sufficiently effective to cause a resolution in their ester methylene proton signals resulting in simplified spectral patterns.

Compound 10 in $CDCl_3$ shows (Table I) an AB pattern for the benzylic protons which experience the long-range asymmetry of the cage moiety and shielding of the cage methyl protons by the benzylic phenyl group. The spectrum of this compound in nitrobenzene shows two singlets for the ester methyl groups, indicating that these groups also experience the cage asymmetry. The spectrum of compound 11 is quite similar to that of compound 10. The spectra of compounds 12 and 13 show an abnormal shielding of

## Table I
## NMR[a] Data for Compounds 4–13



**4**, R = $CH_3$; R′ = R″ = H
**5**, R = $CH_2CH_3$; R′ = R″ = H
**6**, R = $CH_3$; R′ = H; R″ = $CH_3$
**7**, R = $CH_2CH_3$; R′ = H; R″ = $CH_3$
**8**, R = $CH_3$; R′ = $CH_2C_6H_5$; R″ = H
**9**, R = $CH_2CH_3$; R′ = $CH_2C_6H_5$; R″ = H
**10**, R = $CH_3$; R′ = $CH_2C_6H_5$; R″ = $CH_3$
**11**, R = $CH_2CH_3$; R′ = $CH_2C_6H_5$; R″ = $CH_3$
**12**, R = $CH_2CH_3$; R′ = $CH_2CH_3$; R″ = H
**13**, R = $CH_3$; R′ = $CH_2CH_3$; R″ = $CH_3$

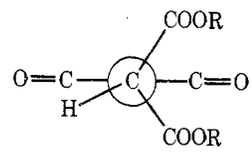
| Compd | Solvent | R | R′ | R″ | $H_{12}$[b] | $H_{10}$ | $H_9$[b] | Aromatic protons |
|---|---|---|---|---|---|---|---|---|
| 4 | $CDCl_3$ | 3.65 (6 H, s) | 5.03 (1 H, s) | 3.35 (1 H, m) | 3.35 (1 H, m) | 4.88 (1 H, m) | 4.88 (1 H, m) | 7.4 (8 H, m) |
| | $C_6H_5NO_2$ | 3.70 (6 H, s) | 5.28 (1 H, s) | 3.62 (1 H, m) | 3.62 (1 H, m) | 5.11 (1 H, m) | 5.11 (1 H, m) | |
| 5 | $CDCl_3$ | 4.21 (4 H, q)[c] 1.22 (6 H, t) | 4.93 (1 H, s) | 3.35 (1 H, m) | 3.35 (1 H, m) | 4.88 (1 H, m) | 4.88 (1 H, m) | 7.4 (8 H, m) |
| | $C_6H_5NO_2$ | 4.28 (4 H, q)[c] 1.22 (6 H, t) | 5.22 (1 H, s) | 3.58 (1 H, m) | 3.58 (1 H, m) | 5.12 (1 H, m) | 5.12 (1 H, m) | |
| 6 | $CDCl_3$ | 3.7 (6 H, ds) 1:1; 2 Hz | 5.0 (1 H, s) | 1.23 (3 H, s) | 2.81 (1 H, d) | 4.48 (1 H, s) | 4.83 (1 H, d) | 7.4 (8 H, m) |
| | $C_6H_5NO_2$ | 3.77 (6 H, ds) 1:1; 2 Hz | 5.24 (1 H, s) | 1.33 (3 H, s) | 3.01 (1 H, d) | 4.68 (1 H, s) | 5.04 (1 H, d) | |
| 7 | $CDCl_3$ | 4.21 (4 H, dq)[d] 1:1; 2 Hz 1.22 (6 H, t) | 4.98 (1 H, s) | 1.22 (3 H, s) | 2.81 (1 H, d) | 4.48 (1 H, s) | 4.83 (1 H, d) | 7.4 (8 H, m) |
| | $C_6H_5NO_2$ | 4.29 (4 H, dq)[d] 1.23 (6 H, t) | 5.17 (1 H, s) | 1.30 (3 H, s) | 2.98 (1 H, d) | 4.65 (1 H, s) | 5.0 (1 H, d) | |
| 8 | $CDCl_3$ | 3.65 (6 H, s) | 3.56 (2 H, s) | 2.90 (1 H, m) | 2.90 (1 H, m) | 4.70 (1 H, m) | 4.70 (1 H, m) | 7.4 (13 H, m) |
| | $C_6H_5NO_2$ | 3.79 (6 H, s) | 3.79 (2 H, s) | 3.15 (1 H, m) | 3.15 (1 H, m) | 4.97 (1 H, m) | 4.97 (1 H, m) | |
| 9 | $CDCl_3$ | 4.17 (4 H, mq)[c] 1.15 (6 H, t) | 3.55 (2 H, s) | 2.87 (1 H, m) | 2.87 (1 H, m) | 4.77 (1 H, m) | 4.77 (1 H, m) | 7.37 (13 H, m) |
| | $C_6H_5NO_2$ | 4.34 (4 H, mq)[c] 1.26 (6 H, t) | 3.79 (2 H, s) | 3.10 (1 H, m) | 3.10 (1 H, m) | 4.97 (1 H, m) | 4.97 (1 H, m) | |
| 10 | $CDCl_3$ | 3.67 (6 H, s) | 3.60 (2 H, q)[e] | 0.69 (3 H, s) | 2.37 (1 H, d) | 4.29 (1 H, s) | 4.72 (1 H, d) | 7.37 (13 H, m) |
| | $C_6H_5NO_2$ | 3.85 (6 H, ds) 1:1; 0.7 Hz | 3.80 (2 H, q)[e] | 0.78 (3 H, s) | 2.49 (1 H, d) | 4.45 (1 H, s) | 4.89 (1 H, d) | |
| 11 | $CDCl_3$ | 4.19 (4 H, mq)[d] 1.18 (6 H, t) | 3.57 (2 H, q)[e] | 0.66 (3 H, s) | 2.38 (1 H, d) | 4.30 (1 H, s) | 4.73 (1 H, d) | 7.35 (13 H, m) |
| | $C_6H_5NO_2$ | 4.36 (4 H, mq)[d] 1.25 (6 H, dt) $J$ = 1 Hz | 3.79 (2 H, q)[e] | 0.73 (3 H, s) | 2.47 (1 H, d) | 4.45 (1 H, s) | 4.91 (1 H, d) | |
| 12 | $CDCl_3$ | 4.28 (4 H, q)[d] 1.21 (6 H, t) | 2.04 (2 H, q)[c] | 3.37 (1 H, m) | | | | |
| | | | 0.09 (3 H, t) | | 3.37 (1 H, m) | 4.90 (1 H, m) | 4.90 (1 H, m) | 7.46 (8 H, m) |
| | $C_6H_5NO_2$ | 4.40 (4 H, q)[d] 1.28 (6 H, t) | 2.27 (2 H, q)[c] | 3.50 (1 H, m) | | | | |
| | | | 0.37 (3 H, t) | | 3.50 (1 H, m) | 5.09 (1 H, m) | 5.09 (1 H, m) | |
| 13 | $CDCl_3$ | 3.35 (6 H, s) | 2.10 (2 H, q)[c] | 1.23 (3 H, s) | | | | |
| | | | 0.27 (3 H, t) | | 2.83 (1 H, d) | 4.50 (1 H, s) | 4.85 (1 H, d) | 7.45 (8 H, m) |
| | $C_6H_5NO_2$ | 3.87 (6 H, s) | 2.31 (2 H, q)[c] | 1.31 (3 H, s) | | | | |
| | | | 0.48 (3 H, t) | | 2.93 (1 H, d) | 4.68 (1 H, s) | 5.04 (1 H, d) | |

[a] Chemical shifts ($\delta$) are recorded in $CDCl_3$ and nitrobenzene ($C_6H_5NO_2$) at 44.5° using $Me_4Si$ as internal reference standard. In case of multiplicities, algebraic mean positions of the signals are given. Parentheses include proton count and the multiplicities abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, ds = double singlet, dt = doublet triplet, and m = multiplet. [b] $J$ between $H_9$ and $H_{12}$ protons was 3.5 Hz. [c] $J$ = 7.5 Hz between ester ethyl protons. [d] $J$ = 7 Hz between ester ethyl protons. [e] $J_{AB}$ = 14 Hz.

the C-methyl (R′) protons and absence of nonequivalence for the ester methylene protons (Table I).

All the spectra discussed above are consistent with the suggestion that the N–C bond rotation in these compounds is free on the NMR time scale.

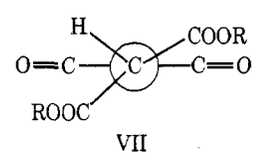
There are certain points which need consideration for comparison between the tetraacylhydrazines and the present system. The N–N′–CO bond angles (~120°) in the tetraacylhydrazine system are fairly larger than the N–C–CO bond angles (~109°) in the present system. Therefore, the nonbonding repulsive forces between any two carbonyl groups, one on either side of the N–C bond, in the transition state would be more than those for the N–N bond system. Then, if it is assumed that the exocyclic malonyl proton pushed toward a carbonyl group of the imide ring (VI)



VI

in compounds **3–7** would not raise considerably the ground-state energy of the molecule, larger barriers could be expected for the N–C bond rotation. Of course, this is not true in the case of compounds **8–11**, where the bulky benzyl group at the exocyclic carbon atom would raise considerably the ground-state energy of the molecule.

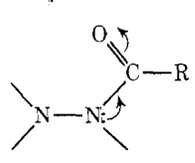
The two *N′*-carbonyls of the tetraacylhydrazine system cross the two imide ring carbonyls simultaneously in the transition state for the rotation, whereby the repulsive forces of the each pair of the crossing carbonyls reinforce those of the other pair. In the present system, two carbonyls at the exocyclic carbon atom cross the two imide ring carbonyls, respectively, one after the other with a difference of about 30° rotation (VII), thereby reducing the bar-



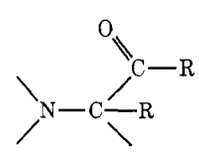
VII

rier height of the N–C bond rotation. Spectral studies of compounds of type IV (R = $CH_3$), which possess only one *N′*-carbonyl group to cross any one of the imide ring carbonyls in the transition state and still show large barriers to rotation (19–21 kcal/mol), indicate that this type of interaction may not be exclusively effective in making the N–C bond rotation free.

A carbonyl group on the hydrazine system lies preferably in the same plane as the N–N bond (VIII) because of delo-

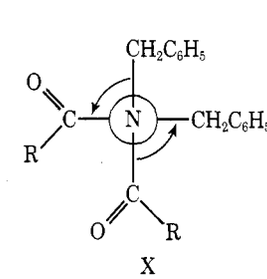


VIII

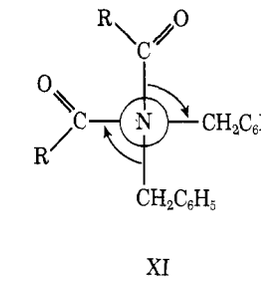


IX

calization of the nitrogen lone pair electrons, and thus the repulsive interactions in the transition state may be greater in this case. This is not the case with the present system, where the exocyclic *C*-carbonyls may assume any conformation (IX) about the C–CO bonds depending upon the stereoelectronic factors in the system. It would be helpful to consider here an acyclic *N,N′*-diacyl-*N,N′*-dialkylhydrazine system. For the interconversion of the two conformational diastereomers X and XI, a carbonyl group on one nitrogen atom may cross the alkyl group on the other nitro-



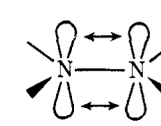
X



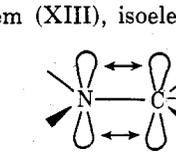
XI

gen atom and crossing of a carbonyl group with the other carbonyl group in the transition state is not a necessary condition. In the present system the two carbonyls of the imide ring lie in the plane of the N–C bond, and therefore, whatever the conformation of the *C*-carbonyls may be, the nonbonding interactions would not be less than those in the *N,N′*-diacyl-*N,N′*-dialkylhydrazine system.

The foregoing data strongly suggest that nonbonding repulsions between the substituents are not the main contribution to the N–N bond torsional barriers. Besides other factors, it may now be considered that the acylhydrazine system of the type discussed above possesses two lone pairs containing p orbitals on the two nitrogen atoms, whereas the present system possesses only one such orbital. Therefore, the main cause of hindrance to the N–N bond rotation seems to be the electrostatic repulsions between the two parallel p orbitals in the transition state (XII). This could be tested by preparing sodium salts of compounds **4** and **6**, which form a >N–⁻C< system (XIII), isoelectronic with



XII



XIII

the N–N bond system. The NMR spectra of both these salts in pyridine show two singlets each of 3 H intensity for their two ester methyl groups, with an internal chemical shift of 16 Hz. This multiplicity of ester methyl signals can be attributed to restricted rotation about the N–C bond, and supports the above conclusions. The barrier to rotation about the N–C bond of the sodium salt of compound **4** has been evaluated to be 20 kcal/mol by VTNMR measurements (solvent quinoline, $\Delta\nu$ at 44.5° = 17 Hz, coalescence temperature 120°) using Eyring's rate equation.[1] It may be mentioned that compound **4** could be regenerated from the sodium salt on acidification, which does not show any multiplicity in pyridine or in nitrobenzene (Table I) for the two ester methyl protons.

## Experimental Section

NMR spectra were recorded on a Varian A-60D spectrometer equipped with a variable-temperature controller (Model V-6040). Ir spectra were recorded in Nujol on a Perkin-Elmer 257 spectrophotometer. Chemical analyses, ir spectra and melting points of all compounds are given in Table II.

**A.** 9,10-Dihydroanthracene-9,10-*endo*-$\alpha,\beta$-succinimide (**14**) was prepared by heating anthracene-maleic anhydride adduct (1 mol) and urea ( a little more than 0.5 mol) in a long-necked round-bottom flask at 140–150° for 1.5 hr. At the end of the reaction, the evolution of ammonia ceased and the boiling reaction mixture turned into a solid. After cooling, the solid mass was disintegrated by addition of water, filtered, and dried. It was recrystallized from hot xylene: mp 322–325° (327°);[14] ir $\nu_{max}$ 1735 s, 1795 m, 3370 s $cm^{-1}$.

9,10-Dihydroanthracene-9,10-*endo*-$\alpha$-methyl-$\alpha,\beta$-succinimide (**15**) was obtained by a similar method using anthracene–citraconic anhydride adduct and urea and was recrystallized from hot ethanol: mp 227–230°; ir $\nu_{max}$ 1720 s, 1777 s, 3086 m, 3160 m $cm^{-1}$.

Bicyclo[2.2.1]-5-heptene-2,3-*endo*-dicarboximide (**16**) was prepared by the method of Morgan et al.:[15] mp 182–184°; ir $\nu_{max}$ 1710 s, 1760 s, 3084 s, 3180 s $cm^{-1}$.

**Table II**
**Melting Points, Elemental Analysis, and Characteristic Infrared[a] Peaks of Compounds 1-13**

| Compd | Mp, °C | Found, % C | Found, % H | Calcd, % C | Calcd, % H | Ir, $\nu_{max}$, $cm^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 75–76 | 58.88 | 4.78 | 59.02 | 4.92 | 1734 s, 1758 s, 1787 w |
| 2 | 109 | 66.48 | 5.27 | 66.83 | 5.32 | 1730 s, 1762 s, 1789 m |
| 3 | 85 | 59.64 | 5.80 | 59.81 | 5.92 | 1710 s, 1745 s, 1760 s, 1733 s, 1756 s, 1790 m |
| 4 | 176–177 | 68.25 | 4.68 | 68.14 | 4.69 | 1710 s, 1747 s, 1760 s, 1785 m |
| 5 | 157–159 | 69.52 | 5.45 | 69.28 | 5.31 | 1717 s, 1744 s, 1782 m |
| 6 | 166–167 | 68.81 | 4.90 | 68.73 | 5.0 | 1718 s, 1750 s, 1780 w |
| 7 | 121–122 | 69.88 | 5.60 | 69.70 | 5.59 | 1710 s, 1748 s, 1782 m |
| 8 | 198–200 | 72.58 | 5.24 | 72.72 | 5.05 | 1708 s, 1722 m, 1748 m, 1760 s, 1780 s |
| 9 | 165–167 | 73.03 | 5.51 | 73.42 | 5.54 | 1712 s, 1753 s, 1778 m |
| 10 | 180–181 | 72.88 | 5.50 | 73.08 | 5.30 | 1715 s, 1744 s, 1764 s |
| 11 | 154–155 | 73.44 | 5.66 | 73.74 | 5.77 | 1713 s, 1752 s, 1778 m |
| 12 | 123–125 | 69.89 | 5.83 | 70.28 | 5.86 | 1720 s, 1754 s, 1773 m, 1790 w |
| 13 | 182–183 | 69.66 | 5.48 | 69.80 | 5.59 | 1722 s, 1748 s, 1766 s, 1788 m |

[a] Ir taken in Nujol medium. Abbreviations: s = strong, m = medium, w = weak.

**B.** Compounds **3–7** were derived from the dicarboximides **14–16**. The imides were converted into their potassium salts by reaction with equimolar proportions of alcoholic potassium hydroxide and were recovered as solids on evaporation. The potassium salts of these imides were mixed with appropriate bromomalonic ester in equimolar amounts and heated at 120° for 1 hr in an oil bath. The reaction mixtures were then cooled to obtain solids which were washed with water to remove the potassium bromide formed in the reaction. The products were recovered by dissolving these solids in cold benzene and discarding the remaining residues (which were supposed to be unreacted starting materials). All the compounds were recrystallized from ethanol. The melting points and characteristic ir bands are given in Table II.

**C. Compounds 8–11.** Compound **8** was obtained by adding an equimolar amount of benzyl chloride to the mixture of compound **4** and anhydrous potassium carbonate in dimethylformamide. The reaction mixture was stirred at room temperature for about 1 hr and thereafter heated at 140° for another 1 hr. The solvent (DMF) was then removed under reduced pressure and the solid mass was triturated with crushed ice. The product was filtered, dried, and recrystallized from ethanol. The other benzyl derivatives **9–11** were obtained by benzylation of appropriate *N*-malonyl compounds **5–7**, under similar conditions. Compounds **12** and **13** were also obtained under similar conditions by reaction of ethyl bromide with compounds **5** and **6**, respectively.

**D. Sodium Salts of Compounds 4 and 6.** Compound **4** dissolved in dry benzene was treated with 1 mol of sodium hydride in dry benzene. The reaction mixture was refluxed for about 1 hr to complete the reaction. White, powdered solid was recovered by removing the solvent under reduced pressure and dried under vacuum.

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**Registry No.**—**1**, 5680-61-5; **2**, 17102-94-2; **3**, 53965-75-6; **4**, 53965-76-7; **5**, 53965-77-8; **6**, 53965-78-9; **7**, 53965-79-0; **8**, 53965-80-3; **9**, 53965-81-4; **10**, 53965-82-5; **11**, 53965-83-6; **12**, 53965-84-7; **13**, 53965-85-8; **14**, 5721-34-6; **15**, 53965-86-9; **16**, 6319-06-8.

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