(Matsumoto, Higuchi, Hoshino, Koike, Naoi & Nagai, 1988), das bisher aber noch nicht strukturell charakterisiert worden ist. Ein bemerkenswerter formaler Zusammenhang besteht mit der Kristallstruktur des Cäsiumsilicids CsSi (Kliche, Schwarz & von Schnering, 1987), das aus durch die Kationen als $\mu_3$-Liganden zu $Cs_4Si_4$-Cubaneinheiten ergänzten $Si_4$-Tetraedern aufgebaut ist und bei Besetzung gleichartiger Lagen in der gleichen Raumgruppe wie die hier beschriebene Verbindung kristallisiert.

Diese Untersuchung entstand in enger Zusammenarbeit mit Frau Professor Dr M. Baudler und Herrn Dipl. Chem. G. Scholz, die uns die Kristalle überlassen und bei der Diskussion der Ergebnisse geholfen haben. Die Arbeit wurde durch eine Sachmittelspende des Fonds der Chemischen Industrie gefördert. Wir danken den Genannten für die Unterstützung.

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*Acta Cryst.* (1990). C**46**, 1074–1077

# Structure of Methyl 4,*exo*-6-Diphenyl-*exo*-2,3-(phenyliminodicarbonyl)-7-azabicyclo[2.2.1]heptane-1-carboxylate*

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(*Received* 3 *August* 1989; *accepted* 14 *September* 1989)

**Abstract.** $C_{28}H_{24}N_2O_4$, $M_r = 452{\cdot}5$, monoclinic, $P2_1/c$, $a = 13{\cdot}321\,(3)$, $b = 14{\cdot}566\,(2)$, $c = 11{\cdot}625\,(2)$ Å, $\beta = 92{\cdot}18\,(2)^\circ$, $V = 2254\,(1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}383$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}084$ mm$^{-1}$, $F(000) = 952$, $T = 294$ K, $R = 0{\cdot}037$ for 2420 unique reflections. The conformation specified in the name of the compound was determined in order to establish the diastereochemistry of the reaction of cyclic azomethine ylides with *N*-phenylmaleimide.

**Introduction.** Following a study of the stereochemistry of 1,3-dipolar cycloadditions, the title

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* Alternative name: methyl 3,5-dioxo-4,7,9-triphenyl-4,10-diazatricyclo[$5.2.1.0^{2,6}$]decane-1-carboxylate.

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0108-2701/90/061074-04$03.00

compound is a product which exemplifies such a reaction of 5-phenyl-2-methoxycarbonyl-3,4-dihydro-2*H*-pyrrole derivatives (1) with *N*-phenylmaleimide. Compounds (1) tautomerize in refluxing toluene to give cyclic azomethine ylides (2), which can react with *N*-phenylmaleimide. In this way Mkhairi & Hamelin (1987) prepared the cycloadduct (3) ($R^4$ = H). Using the same experimental conditions we prepared a similar compound (3) ($R^4$ = Ph) (title compound); the mechanism of this reaction could only be ascertained from the stereochemistry of (3), which could not be obtained from proton magnetic resonance.

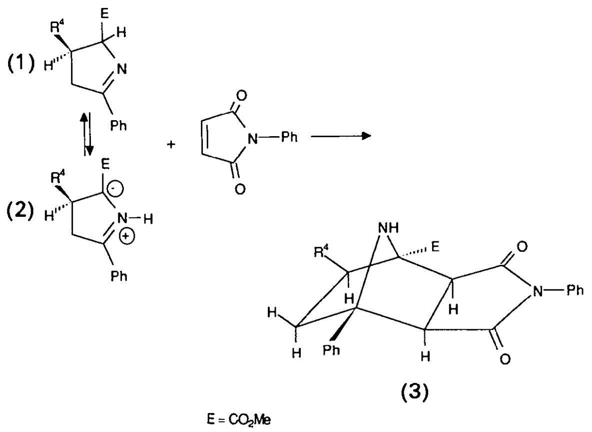

Table 1. *Positional parameters and their estimated standard deviations*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 0·7590 (1) | 0·4166 (1) | 0·4118 (2) | 3·14 (4) |
| C(2) | 0·6650 (1) | 0·4283 (2) | 0·4874 (2) | 3·28 (4) |
| C(3) | 0·7132 (1) | 0·4315 (1) | 0·6100 (2) | 3·27 (4) |
| C(4) | 0·8258 (1) | 0·4170 (1) | 0·5879 (1) | 2·85 (4) |
| C(5) | 0·8392 (1) | 0·3140 (1) | 0·5528 (1) | 3·28 (4) |
| C(6) | 0·7941 (2) | 0·3162 (2) | 0·4288 (1) | 3·71 (5) |
| N(7) | 0·8318 (1) | 0·4712 (1) | 0·4822 (1) | 2·89 (3) |
| C(8) | 0·6128 (1) | 0·5186 (2) | 0·4724 (2) | 3·38 (4) |
| O(8) | 0·5589 (1) | 0·5428 (1) | 0·3913 (1) | 4·21 (3) |
| N(9) | 0·6331 (1) | 0·5725 (1) | 0·5697 (1) | 3·48 (4) |
| C(10) | 0·6915 (1) | 0·5263 (2) | 0·6529 (2) | 3·62 (4) |
| O(10) | 0·7191 (1) | 0·5592 (1) | 0·7439 (1) | 5·32 (4) |
| C(11) | 0·7469 (1) | 0·4470 (2) | 0·2879 (2) | 3·56 (4) |
| C(12) | 0·7816 (2) | 0·5303 (2) | 0·2523 (2) | 5·11 (6) |
| C(13) | 0·7726 (2) | 0·5555 (2) | 0·1371 (2) | 6·98 (7) |
| C(14) | 0·7297 (2) | 0·4970 (2) | 0·0582 (2) | 7·21 (8) |
| C(15) | 0·6932 (2) | 0·4148 (2) | 0·0925 (2) | 6·56 (7) |
| C(16) | 0·7013 (2) | 0·3887 (2) | 0·2070 (2) | 4·91 (5) |
| C(41) | 0·8989 (1) | 0·4465 (1) | 0·6821 (2) | 3·03 (4) |
| O(41) | 0·9681 (1) | 0·4979 (1) | 0·6695 (1) | 3·87 (3) |
| O(42) | 0·8785 (1) | 0·4052 (1) | 0·7803 (1) | 3·81 (3) |
| C(43) | 0·9467 (2) | 0·4251 (2) | 0·8775 (2) | 5·30 (6) |
| C(51) | 0·9466 (2) | 0·2806 (1) | 0·5653 (2) | 3·20 (4) |
| C(52) | 1·0214 (2) | 0·3115 (2) | 0·4954 (2) | 4·05 (5) |
| C(53) | 1·1196 (2) | 0·2822 (2) | 0·5123 (2) | 4·83 (5) |
| C(54) | 1·1444 (2) | 0·2207 (2) | 0·5976 (2) | 4·69 (5) |
| C(55) | 1·0709 (2) | 0·1886 (2) | 0·6674 (2) | 4·80 (5) |
| C(56) | 0·9735 (2) | 0·2182 (2) | 0·6503 (2) | 4·18 (5) |
| C(91) | 0·5942 (1) | 0·6628 (2) | 0·5848 (2) | 3·71 (4) |
| C(92) | 0·6028 (2) | 0·7274 (2) | 0·4992 (2) | 4·92 (6) |
| C(93) | 0·5664 (2) | 0·8146 (2) | 0·5153 (2) | 6·59 (7) |
| C(94) | 0·5225 (2) | 0·8377 (2) | 0·6173 (2) | 6·56 (7) |
| C(95) | 0·5139 (2) | 0·7733 (2) | 0·7005 (2) | 5·99 (6) |
| C(96) | 0·5484 (2) | 0·6852 (2) | 0·6853 (2) | 4·84 (5) |

**Experimental.** Parallelepiped shaped crystal from a toluene solution, 0·27 × 0·30 × 0·50 mm, CAD-4 Enraf–Nonius diffractometer, cell parameters were determined from 25 reflections having $7{\cdot}09 \leq \theta \leq 18{\cdot}57°$, no absorption correction was applied. $0{\cdot}039 \leq (\sin\theta)/\lambda \leq 0{\cdot}572$ Å$^{-1}$; $-16 \leq h \leq 16$, $0 \leq k \leq 18$, $0 \leq l \leq 14$; intensity control reflections: $\bar{4}22$, $2\bar{2}4$, $0\bar{8}0$, 0·7% variation during measurements, average $\sigma(I)/I = 0{\cdot}0054$. 3536 unique reflections, 1116 unobserved reflections [$I < 3\sigma(I)$]. Direct methods, program *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H atoms bonded to C(43) were located from a Fourier difference map. Other H-atom locations were calculated (Frenz, 1982). Atomic diffusion factors were from *International Tables for X-ray Crystallography* (1974). Full-matrix refinements. Refined parameters were $x$, $y$, $z$ for all atoms and $\beta_{ij}$'s for C, N and O atoms. For each H atom $B$ was chosen equal to 1 Å$^2$ + $B$ of the neighbouring heavy atom. $R = 0{\cdot}037$, $wR = 0{\cdot}045$, $w = 1/\sigma^2(F)$, $S = 1{\cdot}66$, maximum shift-to-e.s.d. ratio $(\Delta/\sigma)_{\max} = 0{\cdot}01$, $|\Delta\rho|_{\max} = 0{\cdot}13\,(4)$ e Å$^{-3}$. Program *ORTEP* (Johnson, 1976) was used to represent the molecule (Fig. 1). Atomic coordinates are given in Table 1 and bond distances and angles are given in Table 2.*

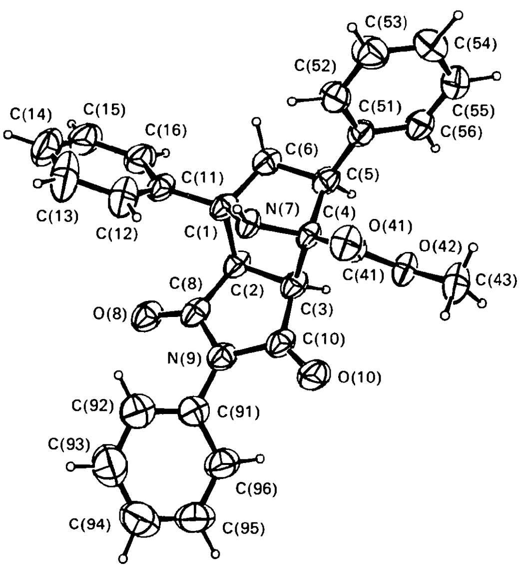

Fig. 1. *ORTEP* view of the molecule.

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* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, bond distances and angles involving H atoms, and data of average planes of the rings have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52666 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·567 (3) | C(12)—C(13) | 1·389 (3) |
| C(1)—C(6) | 1·545 (3) | C(13)—C(14) | 1·363 (4) |
| C(1)—N(7) | 1·478 (2) | C(14)—C(15) | 1·358 (4) |
| C(1)—C(11) | 1·509 (3) | C(15)—C(16) | 1·384 (3) |
| C(2)—C(3) | 1·541 (2) | C(41)—O(41) | 1·200 (2) |
| C(2)—C(8) | 1·494 (3) | C(41)—O(42) | 1·328 (2) |
| C(3)—C(4) | 1·546 (3) | O(42)—C(43) | 1·452 (3) |
| C(3)—C(10) | 1·499 (3) | C(51)—C(52) | 1·385 (3) |
| C(4)—C(5) | 1·567 (3) | C(51)—C(56) | 1·379 (3) |
| C(4)—N(7) | 1·465 (2) | C(52)—C(53) | 1·383 (3) |
| C(4)—C(41) | 1·499 (2) | C(53)—C(54) | 1·368 (3) |
| C(5)—C(6) | 1·541 (3) | C(54)—C(55) | 1·377 (3) |
| C(5)—C(51) | 1·514 (3) | C(55)—C(56) | 1·374 (3) |
| C(8)—O(8) | 1·215 (2) | C(91)—C(92) | 1·377 (3) |
| C(8)—N(9) | 1·396 (2) | C(91)—C(96) | 1·378 (3) |
| N(9)—C(10) | 1·391 (2) | C(92)—C(93) | 1·375 (4) |
| N(9)—C(91) | 1·426 (3) | C(93)—C(94) | 1·384 (4) |
| C(10)—O(10) | 1·206 (2) | C(94)—C(95) | 1·355 (4) |
| C(11)—C(12) | 1·368 (3) | C(95)—C(96) | 1·377 (4) |
| C(11)—C(16) | 1·390 (3) | | |
| C(2)—C(1)—C(6) | 106·0 (2) | C(3)—C(10)—O(10) | 127·0 (2) |
| C(2)—C(1)—N(7) | 98·7 (1) | N(9)—C(10)—O(10) | 124·1 (2) |
| C(2)—C(1)—C(11) | 116·4 (1) | C(1)—C(11)—C(12) | 121·6 (2) |
| C(6)—C(1)—N(7) | 104·4 (1) | C(1)—C(11)—C(16) | 119·6 (2) |
| C(6)—C(1)—C(11) | 114·9 (2) | C(12)—C(11)—C(16) | 118·8 (2) |
| N(7)—C(1)—C(11) | 114·5 (2) | C(11)—C(12)—C(13) | 120·5 (2) |
| C(1)—C(2)—C(3) | 102·0 (1) | C(12)—C(13)—C(14) | 120·2 (3) |
| C(1)—C(2)—C(8) | 114·1 (2) | C(13)—C(14)—C(15) | 120·0 (2) |
| C(3)—C(2)—C(8) | 104·9 (2) | C(14)—C(15)—C(16) | 120·6 (2) |
| C(2)—C(3)—C(4) | 102·5 (1) | C(11)—C(16)—C(15) | 120·0 (2) |
| C(2)—C(3)—C(10) | 104·8 (2) | C(4)—C(41)—O(41) | 124·7 (2) |
| C(4)—C(3)—C(10) | 112·4 (2) | C(4)—C(41)—O(42) | 110·5 (2) |
| C(3)—C(4)—C(5) | 107·1 (2) | O(41)—C(41)—O(42) | 124·8 (2) |
| C(3)—C(4)—N(7) | 98·6 (1) | C(41)—O(42)—C(43) | 115·9 (2) |
| C(3)—C(4)—C(41) | 116·6 (2) | C(5)—C(51)—C(52) | 122·5 (2) |
| C(5)—C(4)—N(7) | 106·7 (1) | C(5)—C(51)—C(56) | 120·0 (2) |
| C(5)—C(4)—C(41) | 112·8 (2) | C(52)—C(51)—C(56) | 117·5 (2) |
| N(7)—C(4)—C(41) | 113·8 (2) | C(51)—C(52)—C(53) | 120·9 (2) |
| C(4)—C(5)—C(6) | 100·3 (2) | C(52)—C(53)—C(54) | 120·4 (2) |
| C(4)—C(5)—C(51) | 113·6 (2) | C(53)—C(54)—C(55) | 119·5 (2) |
| C(6)—C(5)—C(51) | 115·5 (2) | C(54)—C(55)—C(56) | 119·8 (2) |
| C(1)—C(6)—C(5) | 104·2 (2) | C(51)—C(56)—C(55) | 121·9 (2) |
| C(1)—N(7)—C(4) | 96·9 (1) | N(9)—C(91)—C(92) | 120·1 (2) |
| C(2)—C(8)—O(8) | 127·1 (1) | N(9)—C(91)—C(96) | 119·8 (2) |
| C(2)—C(8)—N(9) | 109·0 (2) | C(92)—C(91)—C(96) | 120·2 (2) |
| O(8)—C(8)—N(9) | 123·8 (2) | C(91)—C(92)—C(93) | 119·6 (2) |
| C(8)—N(9)—C(10) | 112·1 (2) | C(92)—C(93)—C(94) | 120·2 (3) |
| C(8)—N(9)—C(91) | 123·9 (2) | C(93)—C(94)—C(95) | 119·5 (3) |
| C(10)—N(9)—C(91) | 123·9 (2) | C(94)—C(95)—C(96) | 121·1 (2) |
| C(3)—C(10)—N(9) | 108·9 (2) | C(91)—C(96)—C(95) | 119·3 (2) |

**Discussion.** Bond lengths obtained for the central part of the compound (the 7-azabicyclo[2.2.1]heptane block) are rather large, as might be expected for cyclic species. For single C—C bonds the average value is 1·551 (12) Å, whereas the average for other C—C single bonds is 1·503 (8) Å. For single C—N bonds the average is 1·47 (1) Å, whereas the average for other C—N single bonds is 1·40 (2) Å.

Numerous bicyclo[2.2.1]heptane compounds have been studied; a few of them are azabicyclo[2.2.1]-heptane derivatives: several 2-aza (Ammon, Mazzocchi & Liu, 1980; Ammon, Mazzocchi, Liu, Colicelli, Doherty & Stewart, 1982; Ammon, Bhattacharjee, Ravi & Potlock, 1983), a 1,4-diaza (Abraham, Rosenstein & Pettit, 1971), a 2,3-diaza (Little & Doedens, 1972), a 5-aza-2-oxa-3-oxo (Lenstra, Petit & Geise, 1979) and a hexahydrotetrazine derivative (Bokii, Babushkina, Vasil'ev, Volodina, Kozik, Struchkov & Suvorov, 1975), but only one paper – to our knowledge – deals with a 7-azabicyclo[2.2.1]-heptane derivative (Swanson, Stavinoha & Mariano, 1982).

Good agreement is found between data in these papers and our results. In the paper by Swanson *et al.* the average C—C single bond in the bridged ring is 1·552 (30) Å and the average C—N single bond in the bridge is 1·52 (2) Å. Nevertheless our results are probably much more accurate than theirs – as far as they may be compared – since these authors were hindered from obtaining a 'good' conventional *R* factor by the heavy thermal agitation of $ClO_4^-$ ions in their crystals.

### *Mean planes of the different rings*

The planarity of the aromatic rings is good as shown in Table 3 (deposited). Planes were defined as follows: Π(1) C(11) to C(16) plus C(1); Π(5) C(51) to C(56) plus C(5); Π(6) C(91) to C(96) plus N(9).

The heptane ring may be examined in two parts, Π(2) and Π(3) plus N(7). Each part is almost planar; the discrepancy is less than 0·02 Å. The angle between Π(2) and Π(3) is 70 (1)°.

The planarity of the pentagonal ring is quite satisfactory too: see Π(7) below. The angle it forms with Π(2) is 10 (1)° and with Π(3) 62 (1)°.

As often occurs, the methyl group of the methoxycarbonyl group is almost coplanar with the carbonyl as shown by the distance of C(8) to Π(4).

Finally it may be noted that Π(5) is approximately normal to the neighbouring Π(2) ring [the angle is 96 (1)°], presumably due to steric effects.

### *Torsion angles*

The following torsion angles were found: N(7)—C(4)—C(5)—C(51) = 93·8 (2), N(7)—C(4)—C(5)—H(5) = − 147·9 (9), H(3)—C(3)—C(4)—N(7) = 159·8 (8), C(10)—C(3)—C(4)—N(7) = − 73·7 (2)°.

The stereochemistry of (3) ($R^4$ = Ph) proves that the approach of the dipolarophile occurs: (*a*) with the *N*-phenylmaleimide ring in an *exo* position, as suggested by Mkhairi & Hamelin; (*b*) on the opposite side of the substituent $R^4$ = Ph (*anti* approach), this substituent lying in an *exo* position.

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*Acta Cryst.* (1990). C**46**, 1077–1079

# Phenyl-Substituted Cyclopropanes. I. *trans*-2-(*p*-Tolyl)cyclopropanoic Acid

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(*Received* 7 *October* 1988; *accepted* 15 *August* 1989)

**Abstract.** $C_{11}H_{12}O_2$, $M_r = 176·215$, orthorhombic, *Pbcn*, $a = 22·197$ (4), $b = 10·104$ (2), $c = 8·595$ (2) Å, $V = 1927·7$ Å$^3$, $Z = 8$, $D_m = 1·18$, $D_x = 1·214$ g cm$^{-3}$; $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·047$ mm$^{-1}$, $F(000) = 752$, $T = 298$ K, $R = 0·067$ and $wR = 0·074$ for 689 unique reflections with $I > 3\sigma(I)$. The crystal structure consists of cyclic —COOH hydrogen-bonded dimers arranged along **a** with the H atoms situated on a twofold axis equidistant from pairs of O atoms. The *p*-tolyl and carboxylate groups adopt bisected positions with respect to the cyclopropyl ring. The observed pattern of ring bond lengths is consistent with conjugative $\pi$-acceptor interactions involving asymmetry parameters $\delta$(tolyl) = −0·009 and $\delta$(COOH) = −0·026 Å.

**Introduction.** The physical and chemical properties and reactivity patterns of cyclopropane are atypical of higher cycloalkanes. Spectroscopic and chemical studies of various substituted cyclopropanes have shown that the cyclopropyl ring is similar to a double bond in many aspects (Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969; Charton, 1970). The ability of cyclopropane to conjugate with adjacent $\pi$ acceptors, *e.g.* carbonyl, cyano, *etc.* (Hoffmann, 1970; Hoffmann & Stohrer, 1971), and its highly effective stabilization of carbonium ions (Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969) are of particular interest to chemists. The effect of substitution on the geometry of cyclopropane has generated widespread interest and numerous theoretical and experimental studies. In particular, for $\pi$-acceptor substituents, the distal ring bond is shortened and vicinal bonds are lengthened. Data for electron-donor substituents are sparse, and the conjugative effects of some substituents are not yet clearly defined (Allen, 1980, 1981). In the case of phenyl substituents they appear to accept electron density from the cyclopropane $3e'$ orbitals in the bisected conformation, but to donate electron density to the $4e'$ orbitals in the (predominant) perpendicular conformation.

This paper presents the X-ray structure of the first of a series of phenylcyclopropanes, undertaken in order to understand the complex conjugative interaction between a phenyl substituent and the cyclopropane ring.

**Experimental.** Density determined by flotation in $CCl_4$/*n*-hexane. Colourless cube, 0·48 × 0·42 × 0·48 mm. Automated four-circle Philips PW 1100 diffractometer. Lattice parameters determined by least-squares procedure applied to the setting angles of 25 strong reflections in the range $6·6 < \theta < 9·3°$. Intensity data to $(\sin\theta)/\lambda = 0·55$ Å$^{-1}$ in the range $0 \le h \le 26$, $0 \le k \le 11$, $0 \le l \le 9$ measured with graphite-monochromated Mo $K\alpha$ radiation; intensities measured by $\theta$–$2\theta$ scans. Three standards monitored every 50 reflections; intensity variation < 1%. Systematic absences proved the space group to be *Pbcn*. After Lp corrections the 1378 initial reflections were reduced to 689 unique data with $I > 3\sigma(I)$. No corrections made for absorption or extinction.

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0108-2701/90/061077-03$03.00