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Structure of Bis(3-acetylamino-1,2,4-triazole-O,N^4)diaquacopper(II) Sulfate Pentahydrate

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Abstract. $[Cu(C_4H_6N_4O)_2(H_2O)_2](SO_4).5H_2O$, $M_r = 537{\cdot}95$, monoclinic, $P2_1/a$, $a = 24{\cdot}834\,(6)$, $b = 8{\cdot}796\,(4)$, $c = 9{\cdot}751\,(4)$ Å, $\beta = 92{\cdot}21\,(2)°$, $V = 2128\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}68$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 30{\cdot}432$ cm^{-1}, $F(000) = 1116$, $R = 0{\cdot}0437$, $wR = 0{\cdot}0619$ for 3183 independent observed reflections. In the mononuclear cation two oxygen atoms and two triazole-N^4 nitrogen atoms, from two *trans*-oriented chelating 3-acetylamino-1,2,4-triazole ligands, are arranged in the equatorial plane of the Cu coordination octahedron. The axial positions are occupied by two water ligands. The distances in the CuN_2O_4 chromophore are: Cu—O(water) = 2·534 (3) and 2·400 (3) Å, Cu—O(carbonyl) = 1·987 (3) and 1·968 (3) Å and Cu—N(triazole-N^4) = 1·933 (3) and 1·944 (3) Å. The complex cations, the sulfate anions and the uncoordinated water molecules are involved in an intricate system of hydrogen bonds.

Introduction. 5-Amino-1*H*-1,2,4-triazole, often incorrectly named 3-amino-1,2,4-triazole (Starova, Franck-Kamenetskaija, Makarskii & Lopyrev, 1978) and many of its derivatives, often produced in bulk quantities, are among the triazole systems that have been claimed frequently in the patent literature as corrosion inhibitors, additives to photographic materials (Cash & Ferguson, 1980; Smith & Luss, 1976), as fungicides or in other biological applications (Bahel, Dubey, Nath & Srivastava, 1984). In many of these cases the combination of such organic ligands with metal ions is present. However, very often the composition of metal coordination compounds with these derivatives is far from clear and X-ray structural evidence is seldom available. The reason for this may be connected with the well known reaction of the 1,2,4-triazole ring with polynucleate metallic ions (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1987; Vreugdenhil, Haasnoot, Reedijk & Spek, 1987) often forming highly insoluble compounds of variable composition (Haasnoot, Vos & Groeneveld, 1977). In this paper the structure of a copper complex is described in which the polynucleation is apparently prevented by the presence of an extended system of hydrogen bonds.

It has been demonstrated that the reaction of 5-amino-1,2,4-triazole with acetylating reagents can give several products, depending on the nitrogen atom(s) that has(have) been acetylated (Staab & Seel, 1959). The end product of thermal rearrangement or of hydrolysis in boiling water of these compounds is 3-acetylamino-1,2,4-triazole (hereafter abbreviated to aat), as investigated by van den Bos (1960). aat reacts in water with copper(II) salts to give crystalline compounds, all with appreciable amounts of solvent. The crystal and molecular structure of the sulfate compound is described in this paper.

Experimental. The compound was prepared by dissolving 2 mmol of $CuSO_4.5H_2O$ and 4 mmol of aat in 20 ml of water, followed by filtration. Blue crystals appeared in the filtrate after several hours.

A crystal approximately 0·15 × 0·20 × 0·23 mm, Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation, 30 reflections ($15{\cdot}0 \le \theta \le 44{\cdot}7°$) for accurate unit-cell parameters; $\omega/2\theta$ intensity scans, 4559 independent reflections with $3 \le \theta \le 70°$, $-30 \le h \le 30$, $0 \le k \le 10$, $0 \le l \le 11$, 3183 reflections with $I \ge 2\sigma(I)$ considered observed, no significant intensity deterioration of standard reflection $\bar{5}22$. Lp correction. Absorption ignored. Patterson and Fourier methods; full-matrix least-squares refinement on F, anisotropic displacement parameters for non-H atoms and isotropic for H atoms (*SHELX*76, Sheldrick, 1976); H-atom positions initially from ΔF synthesis, subsequently refined by least squares. Final $R = 0{\cdot}0437$, $wR = 0{\cdot}0619$; weighting scheme used in the last cycle was $w = 0{\cdot}8051/[\sigma^2(F_o) + 0{\cdot}0104F_o^2]$; $(\Delta/\sigma)_{\max} = 0{\cdot}5$, final $\Delta\rho$ values $\le |0{\cdot}8|$ e Å^{-3}; atomic scattering factors (anomalous dispersion of Cu atom) from *International Tables for X-ray Crystallography* (1974);

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Table 1. *Fractional atomic coordinates* (× 10^4) *with equivalent isotropic thermal parameters for the non-*H *atoms, with e.s.d.'s in parentheses*

$B_{eq} = \frac{8}{3}\pi^2$ trace **U**.

	x	y	z	B_{eq}(Å^2)
Cu	1407 (1)	1000 (1)	3063 (1)	2·56 (2)
S	3921 (1)	390 (1)	2484 (1)	2·66 (2)
O(11)	780 (1)	−318 (3)	3443 (3)	2·81 (6)
O(12)	2046 (1)	2292 (3)	2860 (3)	3·01 (6)
O(2)	3408 (1)	244 (3)	1716 (3)	4·39 (9)
O(3)	4126 (1)	1955 (3)	2392 (3)	3·96 (8)
O(4)	4322 (1)	−636 (3)	1905 (3)	3·91 (7)
O(5)	3852 (1)	16 (4)	3936 (3)	4·11 (8)
O(1w)	1389 (1)	1999 (4)	5499 (3)	3·14 (7)
O(2w)	1436 (1)	265 (4)	698 (3)	3·64 (9)
O(3w)	2057 (1)	2608 (5)	−586 (4)	4·65 (9)
O(4w)	1858 (1)	−2840 (4)	566 (3)	3·77 (8)
O(5w)	538 (1)	1545 (4)	−752 (3)	4·06 (8)
O(6w)	−541 (1)	2122 (4)	−220 (4)	4·11 (9)
O(7w)	832 (2)	−52 (5)	6938 (4)	5·42 (11)
N(11)	2563 (1)	−2111 (4)	4074 (3)	2·91 (8)
N(21)	2126 (1)	−2948 (4)	4452 (3)	2·95 (8)
N(31)	1879 (1)	−641 (4)	3654 (3)	2·49 (7)
N(41)	1199 (1)	−2401 (4)	4398 (3)	2·53 (7)
N(12)	297 (1)	4263 (4)	2049 (4)	3·14 (8)
N(22)	749 (1)	5107 (4)	1887 (3)	3·00 (7)
N(32)	958 (1)	2723 (4)	2518 (3)	2·48 (7)
N(42)	1674 (1)	4525 (4)	2127 (3)	2·72 (7)
C(11)	1729 (1)	−2000 (4)	4164 (3)	2·41 (8)
C(21)	2416 (1)	−763 (5)	3614 (4)	2·66 (8)
C(31)	759 (1)	−1573 (4)	4020 (3)	2·51 (8)
C(41)	227 (1)	−2259 (6)	4318 (5)	3·36 (11)
C(12)	1137 (1)	4125 (4)	2171 (3)	2·45 (8)
C(22)	420 (1)	2865 (5)	2418 (4)	2·77 (9)
C(32)	2094 (1)	3624 (5)	2449 (3)	2·53 (8)
C(42)	2645 (1)	4280 (5)	2332 (5)	3·31 (10)

calculations performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna) with financial support from the University of Parma.*

Discussion. Final atomic coordinates for the non-H atoms are listed in Table 1 and relevant distances and angles in Table 2.

The structure consists of discrete cationic complexes, sulfate anions and molecules of water of crystallization, linked together by an intricate hydrogen-bonding system involving all the relevant potential hydrogen-bond donors. The copper atom (Fig. 1) displays an octahedral arrangement with two axial water molecules and, in equatorial positions, two oxygen and two nitrogen atoms from two *trans*-oriented 3-acetylamino-1,2,4-triazole molecules acting as chelating ligands: the bite angles associated with the six-membered rings are both 88·8 (1)°.

Table 2. *Relevant bond distances* (Å) *and angles* (°) *in* $[Cu(aat)_2(H_2O)_2](SO_4).5H_2O$

In the coordination sphere of Cu			
Cu—O(11)	1·987 (3)	Cu—N(32)	1·944 (4)
Cu—O(12)	1·968 (3)	Cu—O(1w)	2·535 (3)
Cu—N(31)	1·933 (4)	Cu—O(2w)	2·400 (3)
O(11)—Cu—N(31)	88·8 (1)	O(1w)—Cu—N(31)	90·7 (1)
N(31)—Cu—O(12)	88·8 (1)	O(1w)—Cu—N(32)	87·4 (1)
O(12)—Cu—N(32)	88·8 (1)	O(2w)—Cu—O(11)	94·3 (1)
N(32)—Cu—O(11)	93·5 (1)	O(2w)—Cu—O(12)	90·3 (1)
O(11)—Cu—O(12)	175·0 (1)	O(2w)—Cu—N(31)	92·6 (1)
N(31)—Cu—N(32)	177·0 (1)	O(2w)—Cu—N(32)	89·2 (1)
O(1w)—Cu—O(11)	89·2 (1)	O(1w)—Cu—O(2w)	175·3 (1)
O(1w)—Cu—O(12)	86·4 (1)		
In the organic ligands			
N(11)—N(21)	1·373 (4)	N(12)—N(22)	1·360 (4)
N(21)—C(11)	1·313 (4)	N(22)—C(12)	1·315 (4)
C(11)—N(31)	1·352 (5)	C(12)—N(32)	1·358 (5)
N(31)—C(21)	1·340 (4)	N(32)—C(22)	1·342 (3)
C(21)—N(11)	1·314 (5)	C(22)—N(12)	1·314 (6)
C(11)—N(41)	1·390 (4)	C(12)—N(42)	1·381 (4)
N(41)—C(31)	1·352 (4)	N(42)—C(32)	1·338 (4)
C(31)—O(11)	1·241 (4)	C(32)—O(12)	1·245 (5)
C(31)—C(41)	1·491 (4)	C(32)—C(42)	1·494 (4)
C(21)—N(11)—N(21)	111·3 (3)	C(22)—N(12)—N(22)	111·0 (3)
N(11)—N(21)—C(11)	101·3 (3)	N(12)—N(22)—C(12)	102·6 (3)
N(21)—C(11)—N(31)	115·1 (3)	N(22)—C(12)—N(32)	113·9 (3)
C(11)—N(31)—C(21)	103·2 (3)	C(12)—N(32)—C(22)	103·4 (3)
N(31)—C(21)—N(11)	109·0 (3)	N(32)—C(22)—N(12)	109·1 (3)
N(21)—C(11)—N(41)	120·8 (3)	N(22)—C(12)—N(42)	121·8 (3)
N(31)—C(11)—N(41)	124·1 (3)	N(32)—C(12)—N(42)	124·4 (3)
C(11)—N(41)—C(31)	125·4 (3)	C(12)—N(42)—C(32)	125·9 (3)
N(41)—C(31)—O(11)	123·7 (3)	N(42)—C(32)—O(12)	123·3 (3)
N(41)—C(31)—C(41)	116·2 (3)	N(42)—C(32)—C(42)	117·5 (3)
O(11)—C(31)—C(41)	120·1 (3)	O(12)—C(32)—C(42)	119·2 (3)
Cu—N(31)—C(11)	126·6 (2)	Cu—N(32)—C(12)	125·9 (2)
Cu—N(31)—C(21)	130·1 (3)	Cu—N(32)—C(22)	130·7 (3)
Cu—O(11)—C(31)	130·5 (2)	Cu—O(12)—C(32)	131·5 (2)
Hydrogen bonds			
O(1w)···O(7w)	2·699 (6)	O(5w)···O(4^{ii})	2·750 (4)
H(13)···O(7w)	1·85 (5)	H(22)···O(4^{ii})	1·78 (5)
O(1w)···O(5^{i})	2·780 (5)	O(6w)···O(3^{iv})	2·827 (5)
H(14)···O(5^{i})	2·04 (5)	H(23)···O(3^{iv})	1·92 (5)
O(2w)···O(5w)	2·828 (4)	O(6w)···N(22^{v})	2·964 (5)
H(15)···O(5w)	2·05 (5)	H(24)···N(22^{v})	2·06 (5)
O(2w)···O(4w)	2·930 (5)	O(7w)···O($5w^{vi}$)	2·776 (5)
H(16)···O(4w)	1·91 (5)	H(25)···O($5w^{vi}$)	1·84 (6)
O(3w)···O(2^{ii})	2·797 (5)	O(7w)···O(3^{vii})	2·714 (5)
H(17)···O(2^{ii})	1·99 (6)	H(26)···O(3^{vii})	1·66 (5)
O(3w)···O(2w)	2·888 (5)	N(11)···O($1w^{vii}$)	2·734 (4)
H(18)···O(2w)	2·11 (5)	H(1)···O($1w^{vii}$)	1·75 (5)
O(4w)···O($3w^{iii}$)	2·722 (4)	H(41)···O(5^{vii})	2·799 (5)
H(19)···O($3w^{iii}$)	1·83 (5)	H(3)···O(5^{vii})	1·92 (4)
O(4w)···O(2^{iii})	2·849 (4)	N(12)···O(4^{iv})	2·705 (4)
H(20)···O(2^{iii})	1·95 (5)	H(7)···O(4^{iv})	1·81 (5)
O(5w)···O(6w)	2·795 (4)	N(42)···O($4w^{viii}$)	2·820 (5)
H(21)···O(6w)	1·95 (5)	H(9)···O($4w^{viii}$)	1·96 (4)
O(1w)—H(13)—O(7w)	164 (5)	O(5w)—H(22)—O(4^{ii})	169 (4)
O(1w)—H(14)—O(5^{i})	158 (5)	O(6w)—H(23)—O(3^{iv})	175 (5)
O(2w)—H(15)—O(5w)	162 (5)	O(6w)—H(24)—N(22^{v})	167 (4)
O(2w)—H(16)—O(4w)	165 (4)	O(7w)—H(25)—O($5w^{vi}$)	165 (5)
O(3w)—H(17)—O(2^{ii})	158 (5)	O(7w)—H(26)—O(3^{vii})	175 (4)
O(3w)—H(18)—O(2w)	168 (6)	N(11)—H(1)—O($1w^{vii}$)	164 (4)
O(4w)—H(19)—O($3w^{iii}$)	173 (5)	N(41)—H(3)—O(5^{vii})	167 (4)
O(4w)—H(20)—O(2^{iii})	174 (5)	N(12)—H(7)—O(4^{iv})	177 (4)
O(5w)—H(21)—O(6w)	156 (5)	N(42)—H(9)—O($4w^{viii}$)	164 (4)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, -z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, z$; (v) $-x, 1-y, -z$; (vi) $x, y, 1+z$; (vii) $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$; (viii) $x, 1+y, z$.

The four equatorial donor atoms are nearly coplanar [the maximum deviation from the O_2N_2 plane being 0·025 (3) Å for N(31)]. The copper atom is displaced from this plane by 0·054 (1) Å. The Cu—Ow apical bond lengths [2·534 (3) and 2·400 (3) Å] and the equatorial Cu—O distances [1·987 (3) and 1·968 (3) Å] are comparable to the corresponding values found in octahedral copper(II) complexes containing axial water ligands and equatorial carbonyl oxygen atoms (Sletten, 1982). The Cu—N distances [1·933 (3) and

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51549 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·944 (3) Å] are slightly shorter than values found for monodentate N^4-coordinating triazole rings (greater than 2·00 Å) in dinuclear complexes (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983; Haasnoot, Driessen & Reedijk, 1984) or in layered systems (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1986). In dichlorobis(1-ethyl-1,2,4-triazole)copper(II) (Slovokhotov, Struchkov, Polinsky, Pshezhetsky & Ermakova, 1981) and in 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamidecopper dichloride (Bukovec, Golic, Orel & Kobe, 1981), in which the triazole derivatives act as monodentate and chelating ligands respectively, the Cu—N distances from the N^4-coordinated triazole ring range from 1·96 Å upwards. In the latter compound which contains a chelating triazole ligand, the lengthening of the Cu—N^4(triazole) distance with respect to those found in the present work could be attributed to the presence of the usual four-membered chelate bridge instead of the five-membered chelate bridge found in the title compound.

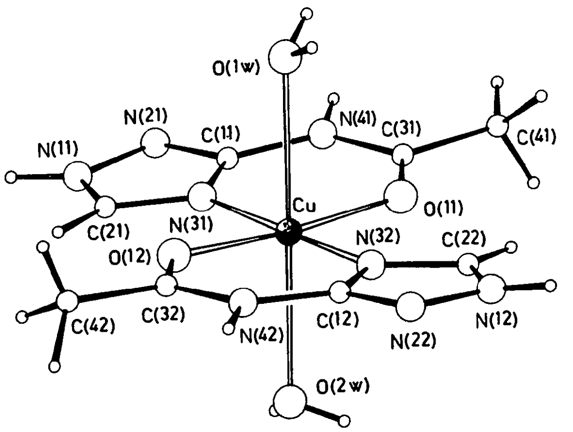

Fig. 1. View of the $[Cu(aat)_2(H_2O)_2]^{2+}$ cationic complex with the atomic numbering scheme.

The bidentate ligands, with the associated triazole rings, are both nearly planar [the maximum deviations from the planes defined by the non-H atoms being 0·112 (3) and 0·035 (3) Å for O(11) and O(12) respectively]. The dihedral angle between the two ligand planes is only 6·9 (1)°. As a result the 3-acetylamino-1,2,4-triazole ligands have a significant π-bonding delocalization (also in accordance with the values found for the bond distances) and the main equatorial portion of the complex can be considered planar, except for the methyl groups.

In the crystal structure four uncoordinated water molecules [containing O(3w)–O(6w)] are held together by hydrogen bonds and are arranged at $z = 0$ in slices parallel to (010) (Fig. 2). Octahedral cations, tetrahedral anions and the remaining O(7w) water molecule of crystallization interpose between these slices. The packing is determined by hydrogen bonds that the interposed species form with water molecules from different slices.

Compared to the parent 5-amino-1,2,4-triazole system (Starova, Franck-Kamenetskaija, Makarskii & Lopyrev, 1978), it appears that the active hydrogen of the ligand has moved to the neighbouring hydrazinic nitrogen so that the acetylamino substituent is on C^3. This change of tautomer may be due to the fact that in 5-amino-triazole very stable double hydrogen bridges exist between neighbouring molecules: N^1—H···N^4 and N^2···H—N(amino). In the present aat—copper com-

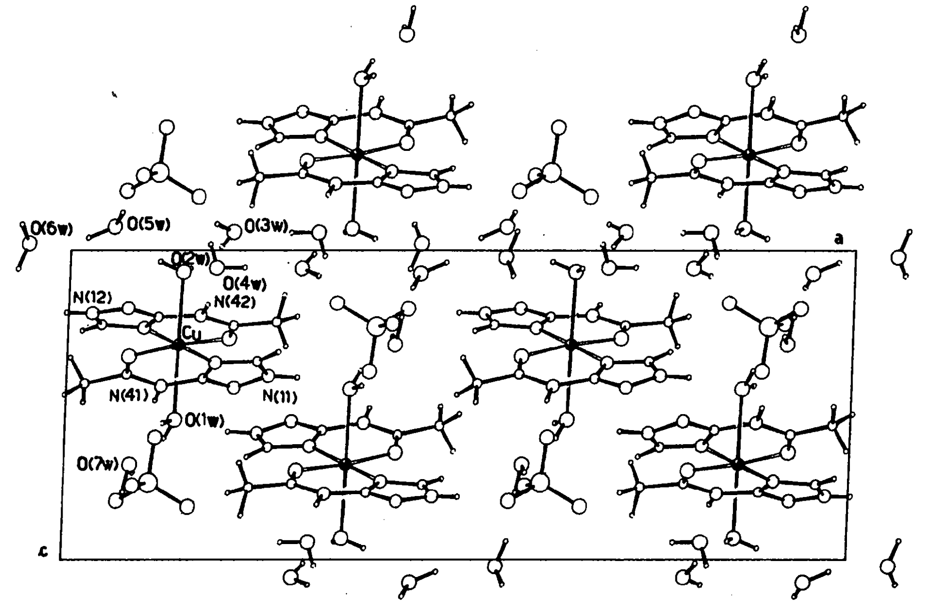

Fig. 2. Projection along **b** of $[Cu(aat)_2(H_2O)_2](SO_4).5H_2O$. The origin is at the upper left vertex of the cell.

pound, however, the N^4 atoms are involved in the coordination of copper and, while all the N^1—H groups contribute to the bridge system, only half of the potential hydrogen-bond acceptor N^2 atoms are involved in hydrogen bridges.

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Structure of 3,4-Bis(phenylthio)cyclobutene-1,2-dione

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Abstract. $C_{16}H_{10}O_2S_2$, $M_r = 298{\cdot}4$, monoclinic, $C2/c$, $a = 19{\cdot}555$ (2), $b = 9{\cdot}082$ (1), $c = 16{\cdot}719$ (2) Å, $\beta = 109{\cdot}0$ (3)°, $V = 2808$ (5) Å^3, $Z = 8$, $D_m = 1{\cdot}400$ g cm^{-3}, $D_x = 1{\cdot}411$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}23$ cm^{-1}, $F(000) = 1232$, $T = 293$ K, final $R = 0{\cdot}050$ for 1925 observed reflexions $[I > 2{\cdot}5\sigma(I)]$, 3387 unique reflexions. The lack of reactivity of the title compound in Diels–Alder cycloadditions is related to the steric hindrance at the C—C double bond. The molecule has a non-symmetric conformation, the two phenyl rings being almost orthogonal to the cyclobutenedione ring.

Introduction. Vinyl sulfides geminally substituted with electron-withdrawing groups are usually very reactive dienophiles in Diels–Alder cycloadditions (De Lucchi & Pasquato, 1988). Their reactivity is higher not only with respect to vinyl sulfide but also with respect to electron-deficient olefins (De Lucchi & Pasquato, 1988; Knapp, Lis & Michna, 1981; Boucher & Stella, 1986). Following our interest in the reactivity of sulfur-substituted olefins in Diels–Alder reactions, we have synthesized the hitherto unknown bis(phenylthio)cyclobutenedione [(1), R = SPh] and tested its reactivity in [4 + 2] cycloaddition reactions. Surprisingly, compound (1) proved to be unreactive in Diels–Alder cycloaddition, also with very reactive dienes such as cyclopentadiene or butadiene (generated *in situ* from 3-sulfolene), and even in the presence of Lewis acids ($AlCl_3$), in contrast to the corresponding electron-deficient olefin, *i.e.* cyclobutene-1,2-dione [(2), R = H], which is a very reactive dienophile, because of

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